

California Regional Water Quality Control Board  
San Diego Region

**THE EFFECTS OF COPPER-BASED ANTIFOULING PAINTS  
ON WATER QUALITY IN RECREATIONAL BOAT MARINAS  
IN SAN DIEGO AND MISSION BAYS**

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by

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## TABLE OF CONTENTS

CHAPTER	PAGE
LIST OF TABLES .....	iv
LIST OF FIGURES .....	v
EXECUTIVE SUMMARY .....	1
I. INTRODUCTION .....	3
Background .....	6
II. UNDERWATER HULL CLEANING STUDY .....	9
Contaminant Concentrations Results .....	12
Hull Cleaning Site .....	12
Contaminant Plume .....	17
Toxicity Analysis .....	17
Test Procedures .....	17
Bioassay Results .....	19
Survival .....	19
Normality .....	22
III. AMBIENT CONCENTRATIONS STUDY .....	24
Sampling Sites .....	24
Analyses .....	24
Results .....	26



CHAPTER	PAGE
IV. TIDAL INFLUENCE STUDY .....	32
Results .....	32
V. CONCLUSIONS .....	40
Underwater Hull Cleaning .....	40
Ambient Concentrations .....	42
Tidal Influence .....	44
General Conclusions .....	44
REFERENCES .....	46



## LIST OF TABLES

TABLE		PAGE
Table I:	Total and Dissolved Metals Concentrations in Underwater Hull Cleaning Samples .....	13
Table II:	Copper Concentrations in San Diego Bay Marinas on June 14, 1994 .....	27
Table III:	Copper Concentrations in San Diego Bay Marinas on June 18, 1994 .....	28
Table IV:	Copper Concentrations in Mission Bay Marinas on June 29, 1994 .....	30
Table V:	Average Copper Concentrations in San Diego and Mission Bays .....	31
Table VI:	Tide Table, June 14, 1994 .....	32
Table VII:	Hourly Dissolved Copper Concentrations .....	33
Table VIII:	Hourly Dissolved Zinc Concentrations .....	37





## LIST OF FIGURES

FIGURE	PAGE
Figure 1: General Location of Sampling Sites and Current Direction in the Underwater Hull Cleaning Study .....	10
Figure 2: Location of Samples Collected within the Test Site Area .....	11
Figure 3: Total Copper vs. Dissolved Copper in Samples Collected in the Underwater Hull Cleaning Study .....	14
Figure 4: Dissolved Copper Concentrations before, during, and after an Underwater Hull Cleaning Operation .....	15
Figure 5: Dissolved Zinc Concentrations before, during, and after an Underwater Hull Cleaning Operation .....	16
Figure 6: Copper Concentrations in Plume and Reference Samples from the Underwater Hull Cleaning Study .....	18
Figure 7: Dissolved Copper NOECs for Survival and Normality in the Underwater Hull Cleaning Study .....	20
Figure 8: Copper Dose Response in Underwater Hull Cleaning Study .....	21
Figure 9: Zinc Dose Response in Underwater Hull Cleaning Study .....	23
Figure 10: Regions of San Diego Bay Sampled in the Ambient Concentrations Study .....	25
Figure 11: Regression Analysis of Dissolved Copper vs. Time .....	35
Figure 12: Dissolved Copper Concentrations vs. the Tidal Cycle .....	36
Figure 13: Regression Analysis of Dissolved Zinc vs. Time .....	38
Figure 14: Dissolved Zinc vs. the Tidal Cycle .....	39



## EXECUTIVE SUMMARY

Since 1993, staff of the California Regional Water Quality Control Board, San Diego Region (RWQCB) have undertaken three studies related to copper concentrations in recreational marinas: The Underwater Hull Cleaning Study (June 1993), the Ambient Concentrations Study (June 1994), and the Tidal Influence Study (June 1994). The purpose, design, results, and conclusions of these studies are contained in this report.

In general, the purpose of the three studies was to examine and elucidate the impacts that the harborage and in-water maintenance of recreational boats is having on the water quality and marine habitat beneficial uses of San Diego and Mission Bays. These studies were designed to: (1) estimate the impact underwater hull cleaning operations have on copper concentrations, (2) estimate the toxicity associated with underwater hull cleaning operations, (3) determine ambient copper concentrations in the yacht harbors of San Diego and Mission Bays, (4) determine if there is any toxicity resulting from the ambient conditions in the yacht harbors, and (5) evaluate the effect of the tidal cycle on ambient copper concentrations in a San Diego Bay yacht harbor.

The most notable findings of these studies include: (1) an underwater hull cleaning operation, carried out by a professional diver using best management practices, caused water column concentrations of copper to rise to levels which greatly exceed U.S. EPA Ambient Water Quality Criteria (for protection of saltwater aquatic life), but then quickly returned to pre-cleaning background levels; (2) most of the copper released during the hull cleaning operation was in the dissolved form; (3) ambient concentrations of dissolved copper in the marinas of both San Diego and Mission Bays were found to exceed U.S. EPA Ambient Water Quality Criteria (saltwater), yet no apparent toxicity was observed in the very sensitive bivalve larvae bioassays; (4) there was no obvious trend in dissolved copper concentration attributable to tidal cycle; (5) although dissolved zinc was found in detectable levels in most

water samples, it was never found in excess of the U.S. EPA Ambient Water Quality Criteria (saltwater) for zinc; and (6) the concentration of dissolved copper was always higher in the marina areas than in or near the main channel of San Diego Bay.

Because the boat used in the Underwater Hull Cleaning Study was not heavily fouled and the professional diver used best management practices in the hull cleaning, the study results may underestimate the impacts of less environmentally sensitive cleaning practices. The cleaning of more heavily fouled boats using more vigorous removal techniques could result in the release of substantially greater concentrations and quantities of copper to the surrounding environment.

In contrast, the actual impact to bay waters from a hull cleaning operation would not be expected to be as great as that exhibited in the bioassays which were performed in the hull cleaning study. While the chronic toxicity tests used in the RWQCB studies are clearly appropriate for an evaluation of ambient conditions, (where long term exposure can be assumed), the tests are less appropriate for an evaluation of the effects of underwater hull cleaning. The hull cleaning samples were collected from within the contaminant plume as it came off the boat, and thus the samples discount the effects of dilution and dispersion. For the results of the hull cleaning bioassays to be directly applicable to real marina conditions, the plume resulting from a hull cleaning operation would have to remain intact and the organisms would have to be in constant exposure to the plume for 48 hours (the duration of the bioassays).

## CHAPTER I

### INTRODUCTION

Section 13240 of the California Water Code mandates the designation of beneficial uses by the California Regional Water Quality Control Board, San Diego Region (RWQCB) for the waters within its jurisdiction. Beneficial uses are the uses of water necessary for the survival and well being of man, plants, and wildlife. These uses of water serve to promote the tangible and intangible economic, social, and environmental goals of mankind (RWQCB, 1994). The designation of beneficial uses is the foundation upon which water quality objectives are based and programs that maintain or enhance water quality are built. Section 13240 also requires the RWQCB to formulate and adopt a Water Quality Control Plan which not only designates beneficial uses but also establishes such water quality objectives which in its judgement will ensure reasonable protection of beneficial uses in the Region. Regrettably, some beneficial uses can be in conflict with others. In many instances, protection or enhancement of one beneficial use curtails the protection, and especially the enhancement, of other competing beneficial uses. As such, the RWQCB must be vigilant to prevent this dichotomy from producing inequities in the treatment of beneficial uses in any water body.

A current manifestation of the dichotomy of beneficial use designations is the apparent conflict between recreational use designations and habitat use designations. The Contact Water Recreation (REC-1) designation covers recreational uses of water involving body contact, including but not limited to: swimming, water skiing, fishing, and SCUBA diving. The Non-contact Water Recreation (REC-2) designation covers recreational uses involving proximity to water, but where body contact is not usually expected, including but not limited to: boating, hiking, and hunting. Habitat use designations cover a wide range of habitat types, including but not limited to: marine, estuarine, and wildlife. Recreation and habitat use designations can enhance or impinge upon one another. Marine life study and sightseeing recreational uses are usually enhanced by habitat use designations, whereas boating and other invasive recreational uses must often be restricted in order to maintain the full function of habitat uses.

San Diego Bay and Mission Bay are two examples of water bodies where there is competition among beneficial uses. The designated beneficial uses of San Diego Bay are: REC-1; REC-2; Industrial Service Supply (IND); Navigation (NAV); Commercial and Sport Fishing (COMM); Preservation of Biological Habitats of Special Significance (BIOL); Estuarine Habitat (EST); Wildlife Habitat (WILD); Rare, Threatened or Endangered Species (RARE); Marine Habitat (MAR); Migration of Aquatic Organisms (MIGR); and Shellfish Harvesting (SHELL)(RWQCB, 1994). The designated beneficial uses of Mission Bay are: REC-1, REC-2, IND, COMM, EST, WILD, RARE, MAR, MIGR, and SHELL (RWQCB, 1994). Portions of both San Diego Bay and Mission Bay have been developed into marinas to facilitate and support recreational boating. The marina development has served to promote and enhance REC-1 and REC-2 beneficial uses in these bays. While the recreational and economic benefits of existing and future marinas are apparent, these marinas may adversely impact the habitat beneficial uses of these same bays.

In addition to the many physical impacts to marine habitats which occur with the construction of a marina, a significant concern of active marinas is the use of antifouling paints on the boats in the marinas. Antifouling paints are applied to the hulls of boats to deter the attachment and growth of attached aquatic organisms. Attached aquatic organisms can promote hull corrosion and significantly increase the drag of a boat, reducing both maneuverability and safety (Gerchacov and Udey, 1984; Loeb *et al*, 1984). The increased drag resulting from excessive fouling of boat hulls can also greatly diminish fuel economy (Preiser and Laster, 1981; Ludgate, 1987). The majority of antifouling paints have a chemical constituent that is toxic to fouling organisms. Once applied, the paint slowly releases this chemical, producing a concentration that deters the propagation of fouling organisms on the boat hull. Unfortunately, the chemical pesticides utilized in the hull paints are not specific to the fouling community and do not remain solely in the direct vicinity of the boat hulls (Anderson and Dalley, 1986; Mellouki *et al*, 1989; Fischer *et al*, 1984). The magnitude of the impact that antifouling paint can have on the surrounding ecosystem is dependent on the concentration, immediate toxicity, and long term bioavailability of the pesticide in the paint.

Prior to the early 1960's, antifouling paints were typically copper based, with cuprous oxide being the most prevalently used active ingredient. In the early 1960's, the drive to find a more effective, efficient antifouling paint led to the use of compounds having tributyltin (TBT) as the active ingredient (Ludgate, 1987).

In 1988, after an increasing body of evidence indicated that the use of tributyltin compounds in antifouling paints was deleteriously affecting the marine ecosystems in both commercial and recreational harbors, the state of California banned the use of TBT-based paints on all boats except those that were either larger than 82 feet or had aluminum hulls (Conway and Locke, 1994). The TBT issue brought the concept of antifouling paints under closer scrutiny by both the general public and the regulatory agencies. At the same time that industries and municipalities were being required to monitor and reduce the presence of all harmful pollutants within their stormwater runoff, antifouling paints were being actively marketed to boat owners on the basis of their superior toxic properties.

After the ban on TBT, many of the boat builders, owners, and boatyards returned to the use of copper-based antifouling paints. While not as toxic as TBT, copper is still toxic at quite low concentrations. There has been increasing concern that the increased use of copper-based antifouling paints may also be seriously impacting the marine ecosystems. Claisse and Alzieu (1993) discovered that since antifouling paint regulations banning TBT were adopted in France in 1982, copper concentrations have increased in adult oysters collected in the proximity of marinas in the Bay of Arcachon, France. While the oyster populations analyzed in their study had not been deleteriously affected by the increased copper concentrations, the authors were concerned about the upward trend.

Many of the recreational marinas in the San Diego region are in areas with restricted tidal flushing. The use of copper-based antifouling paints on boats in these marinas, coupled with their poor tidal flushing characteristics, creates an environment in which copper concentrations may become elevated to levels that are harmful to aquatic organisms throughout the marina. In a 1990 study, Johnston noted an increasing copper gradient from

the entrance of Shelter Island Yacht Harbor towards the moored vessels. Along this copper gradient, he found a decrease in species diversity. The RWQCB staff has been concerned that the harborage and maintenance of recreational boats in San Diego Bay and Mission Bay may be deleteriously affecting aquatic organisms.

### Background

Copper contamination in coastal embayments is a complicated issue. Copper contamination in San Diego Bay is the result of both point and non-point source pollution. Significant historical point source discharges of copper to the water and sediment of San Diego Bay have come from many industrial facilities, such as aeronautical manufacturing companies, power stations, and boatyards/shipyards. Also, in the early 1980's, copper ore was loaded onto ships at the 24th Street Terminal. A significant quantity of ore was spilled into the bay near the bulkhead of that terminal. Cleanup of the spilled copper ore was completed in 1994.

Although sediments in most areas of San Diego Bay contain elevated levels of copper, a Naval Ocean Surveillance Center study of benthic flux in the Shelter Island Yacht Harbor indicated that the geochemical conditions of the sediments in that harbor contribute to the uptake of copper, not its release (Reimer, 1992). Hence, elevated sediment levels may not necessarily contribute to elevated water column concentrations, and should be evaluated on a site by site basis.

Current non-point sources of copper to water in San Diego Bay include municipal storm water run-off and storm water run-off from adjacent industrial and naval facilities (Vanderweele and Ford, 1994). Passive leaching from antifouling paints on boat hulls can also be a significant non-point source of copper contamination. In 1979, Young *et al* estimated that the amount copper discharged from boat hulls in Southern California was at least twice the amount entering coastal waters from stormwater runoff and aerial fallout.

An additional source of copper is generated by the manual or mechanical cleaning of boat hulls while the boats are moored in the water (Conway and Locke, 1994). Since antifouling paints are not one hundred percent effective, attached organisms must be periodically



removed by either in-water hull cleaning or at an appropriately permitted boatyard. Recent studies have indicated that the underwater cleaning of recreational boat hulls can release substantial quantities of copper into the surrounding environment (Litton, 1991). The extent of the release in both concentration and total load is unknown.

In order to evaluate the magnitude of the impact that both the harborage and active in-water maintenance of recreational boats is having on the waters of San Diego and Mission Bays, information on current ambient copper concentrations is needed for these bays. Several investigators have collected data on dissolved copper concentrations in San Diego Bay. In 1978, Zirino *et al* found copper concentrations in San Diego Bay water in the range of 0.7 ug/L to 3.6 ug/L. Zirino *et al* also found that copper concentrations in the bay were influenced by the tidal cycle with greater concentrations occurring during low tides. Also in 1978, Kenis *et al* found copper concentrations in San Diego Bay in the range of 0.7 ug/L to 2.4 ug/L. In 1980, Krett Lane found copper concentrations in the naval region and the Shelter Island Yacht Basin in the range of 2.2 ug/L to 23.0 ug/L with an average concentration of 4.0 ug/L. In 1990, Johnston found an increasing copper concentration gradient in Shelter Island Yacht Harbor with copper concentrations of 2.6 ug/L at the Naval Ocean Surveillance Center and 8.9 to 11 ug/L along the gradient. Johnston also found that tidal change was a major source of the variability in copper concentrations. Valkirs *et al*. (1994) found copper concentrations in San Diego Bay to be similar to levels found in the aforementioned studies. In 1991, Valkirs found copper concentrations in the range of 2.0 ug/L to 5.8 ug/L. In 1992, Valkirs found copper concentrations in the range of 1.9 ug/L to 6.9 ug/L. In 1993, Valkirs found copper concentrations in the range of 2.0 ug/L to 6.2 ug/L. The highest values recorded in Shelter Island Yacht Basin and Glorietta Bay in the Valkirs study were 6.9 ug/L and 5.6 ug/L, respectively. The Krett Lane and Johnston studies indicated that elevated copper concentrations affected species diversity, but did not reduce biomass. The Valkirs study found no toxicity associated with ambient copper concentrations.

The U.S.EPA's Ambient Water Quality Criteria for the protection of saltwater aquatic life is 2.9 ug/L for copper. More specifically, saltwater aquatic organisms and their uses should not

be affected unacceptably if the 1-hour average concentration of copper does not exceed 2.9 ug/L more than once every three years, on average. For waste discharges, the criteria is to be based on the measurement of total recoverable copper. Basing the criteria on the extremely rigorous total recoverable method of analysis may likely overestimate the biological availability and toxicity of the species of the metal which is actually present in any given water sample. Therefore, in most cases, the water quality criteria of 2.9 ug/l will be overprotective if the copper is measured as total recoverable (EPA, 1985). The toxicity of copper in marine systems is most commonly attributed to the free cupric ion ( $\text{Cu}^{2+}$ ), not organic or inorganic complexes (Belli and Zirino, 1993; Zamuda and Sunda, 1982; Sunda and Guillard, 1976; Flemming and Trevors, 1989). Although dissolved copper concentration, as determined by graphite furnace atomic absorption, is not a direct measure of cupric ion concentration - ( i.e. dissolved copper is commonly considered that fraction which can pass through a 0.45 um filter, and as such, might also contain particulate copper smaller than 0.45 um, which may not be bioactive) - dissolved copper is certainly a more realistic reflection of possible bioavailability and toxicity than are measurements of total recoverable copper.

Since 1993, the San Diego RWQCB has undertaken three studies related to copper concentrations in recreational marinas: the Underwater Hull Cleaning Study (June 1993), the Ambient Concentrations Study (June 1994), and the Tidal Influence Study (June 1994). The purpose of these studies was to examine and elucidate the impacts that the harborage and maintenance of recreational boats is having on the water quality and the marine habitat beneficial uses of San Diego and Mission Bays. Specifically, the Underwater Hull Cleaning Study was designed to: (1) estimate the impact underwater hull cleaning operations have on copper concentrations, and (2) estimate the toxicity associated with underwater hull cleaning operations. The Ambient Concentrations Study was designed to: (1) determine ambient copper concentrations in the yacht harbors of San Diego and Mission Bay, and (2) determine if there is any toxicity resulting from the ambient conditions in the yacht harbors. The aim of the Tidal Influence Study was to evaluate the effect of the tidal cycle on ambient copper concentrations in yacht harbors. The design and results of these studies are summarized in this report.

## CHAPTER II

### UNDERWATER HULL CLEANING STUDY

In June of 1993, a study of an underwater hull cleaning operation was conducted in the Shelter Island Yacht Basin of San Diego Bay. The purpose of the study was to identify both the concentration of chemicals which were released into the water and the potential biological effects of those concentrations. Water samples were taken prior to, throughout, and following the physical cleaning of a boat hull and were measured for trace metals by Truesdail Laboratories, Inc., Tustin, California and tested for chronic bivalve toxicity by Ogden Environmental and Energy Services, San Diego, California. To improve detection limits, the chemical analyses included an MIBK extraction followed by graphite furnace atomic absorption.

Three regions were sampled during the hull cleaning test: (1) the area directly around the boat, (2) an area two piers southeast of the boat, and (3) an area within the contaminant plume (Fig. 1 and Fig. 2). The site two piers southeast of the boat was to serve as a reference site. The location of the plume sampling was south of the test site and west of the reference site. The test site was sampled prior to the initiation of the cleaning operation at depths of 3' and 12'. The reference site was also sampled at these same depths prior to the initiation of the hull cleaning. These samples provide an estimation of the background levels of trace metal contaminants. The vessel used in this test was selected to be representative of a typical, properly maintained vessel, with a typical level of fouling growth (Fig. 2).

The cleaning of the hull took approximately 25-30 minutes. During the cleaning, samples were taken every five minutes from the cloudy plume directly around the diver performing the cleaning. Because these samples were taken from different locations around the test boat, contaminant concentrations in each sample were independent of each other. The contaminant concentrations in these samples were dependent on the extent of hull fouling and the degree of exertion by the diver.

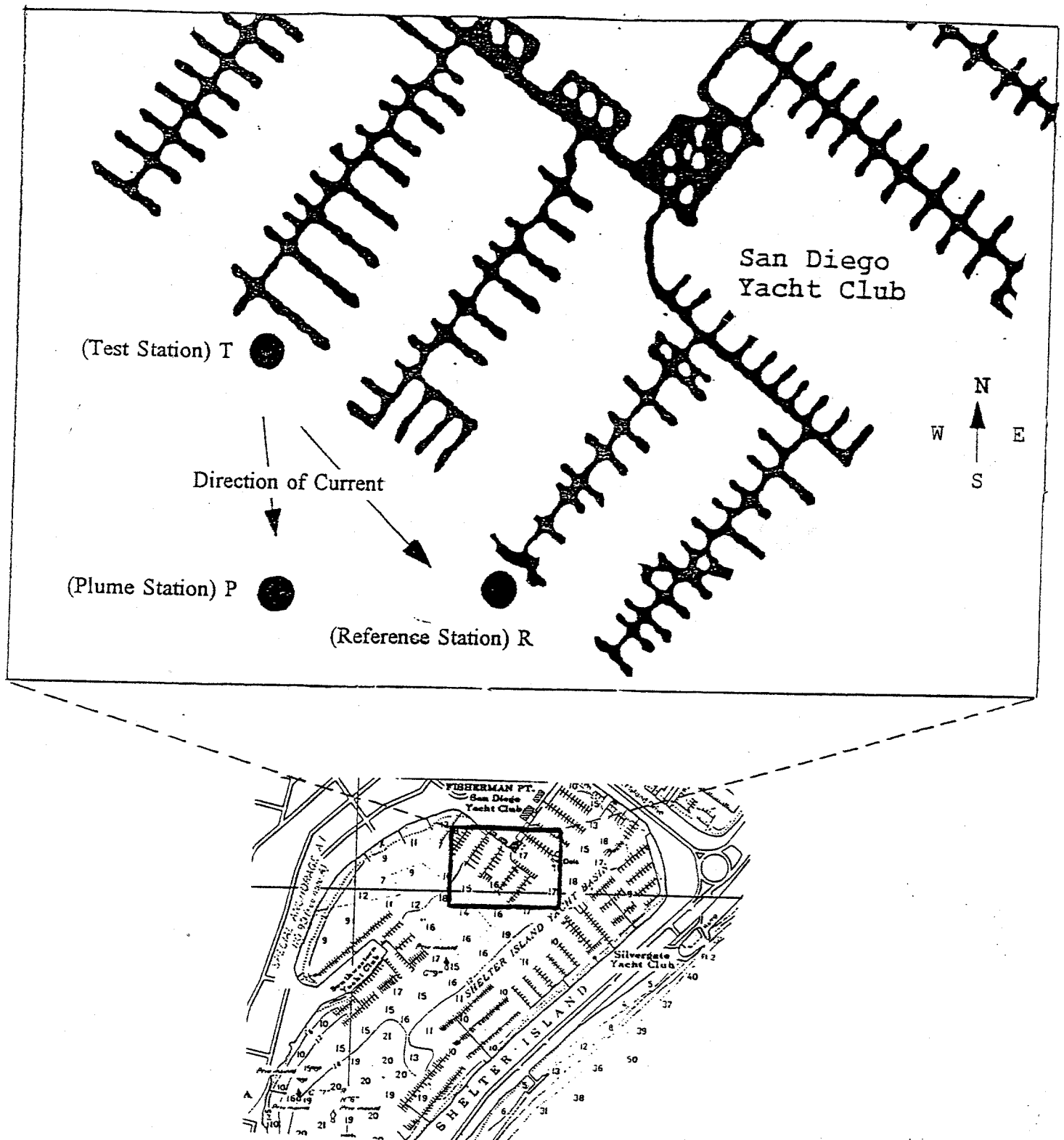
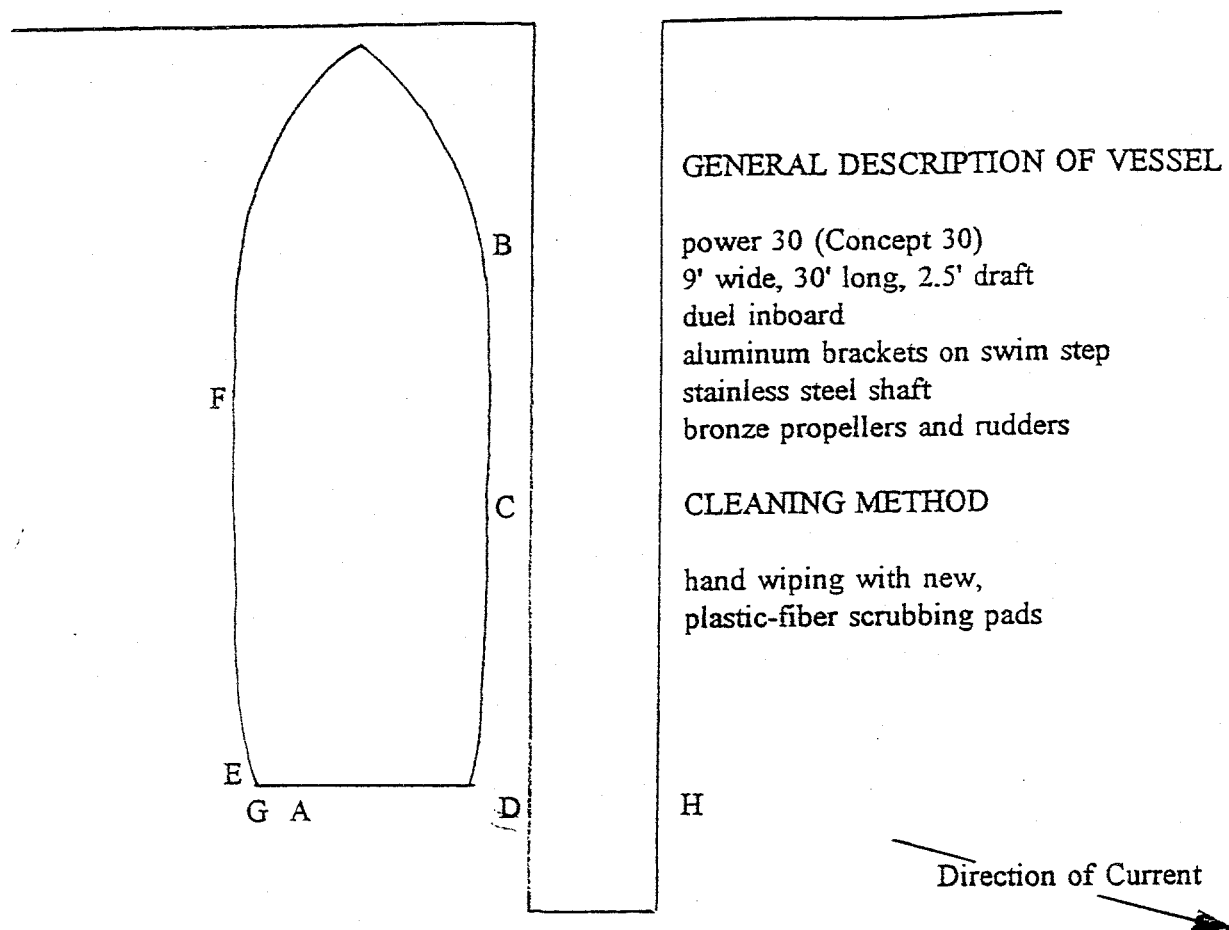


Figure 1: General Location of Sampling Sites and Current Direction in the Underwater Hull Cleaning Study



Location of Samples:

A = TA5-3-1000 and TA5-12-1000  
 B = T-1025  
 C = T-1030  
 D = T-1035  
 E = T-1040  
 F = T-1045  
 G = T-1050  
 H = T-1055, T-1100, T-1115-8, and T-1120

Figure 2: Location of Samples Collected within the Test Site Area

After the cleaning operation ceased, three more samples were collected from a location approximately six feet down current from the test boat (Fig. 2). These samples were taken intermittently for thirty minutes to estimate the rate of return to background concentrations. Plume samples were also taken thirty five minutes after the beginning of the cleaning operation at depths of 3' and 12' (Fig. 1). Movement of the plume was determined by the use of a combination float and sea anchor, which was released near the test boat at the beginning of the hull cleaning operation.

### **Contaminant Concentrations Results**

Of the nine trace metals which were analyzed, only copper and zinc were found consistently in the samples. The other metals were most frequently below detection limits (Table I). The majority of copper and zinc was in the dissolved form. A regression analysis comparing total and dissolved copper yields a linear best fit line with a slope of .94, indicating that the ratio between total and dissolved copper concentrations is nearly 1:1 (Fig. 3). The correlation coefficients for comparisons of total copper to total zinc and for dissolved copper to dissolved zinc were .26 and .27, respectively. These weak correlations indicate that through the course of the hull cleaning study, zinc and copper concentrations were unrelated.

### **Hull Cleaning Site**

Dissolved copper concentrations increased dramatically during the hull cleaning (Fig. 4). Prior to the cleaning, background levels of dissolved copper ranged from 6 ug/L to 16 ug/L, with a mean of 12 ug/L. During the active hull cleaning, levels of dissolved copper ranged from 40 ug/L to 83 ug/L, with a mean of 56 ug/L. The samples taken after the hull cleaning procedure was finished, indicate that the water near the boat rapidly returned to background levels. After five minutes the dissolved copper concentration was 17 ug/L. After ten minutes the dissolved copper concentration was 12 ug/L. While dissolved zinc concentrations did increase moderately during the cleaning operation (Fig. 5), the U.S. EPA's Ambient Water Quality Criteria for the protection of saltwater aquatic life of 95 ug/L for zinc, was never exceeded. Zinc background levels in the area directly around the boat ranged from 24 ug/L to 58 ug/L. Zinc concentrations during the cleaning procedure remained within this range, with an average level of 37 ug/L.

Table I: Total and Dissolved Metals Concentrations in Underwater Hull Cleaning Samples

		Detection Limits	RA1-3-940	RA1-12-940	TA5-3-1000	TA5-12-1000	T-1025	T-1030	T-1035	T-1040	T-1045
<b>Total Metals (ug/L)</b>											
Arsenic	5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Cadmium	1		ND	ND	ND	ND	5	ND	ND	ND	ND
Chromium	5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	5		15	12	16	15	49	83	53	43	82
Lead	3		ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel	10		ND	ND	ND	ND	ND	ND	ND	ND	ND
Mercury	0.5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Silver	1.5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Zinc	10		30	41	39	56	45	45	38	45	41
<b>Dissolved Metals (ug/L)</b>											
Arsenic	5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Cadmium			ND	ND	ND	ND	ND	ND	ND	ND	ND
Chromium	5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	5		13	7	16	10	47	83	48	40	78
Lead	3		ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel	10		ND	ND	ND	ND	ND	ND	ND	ND	ND
Mercury	0.5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Silver	1.5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Zinc	10		29	16	24	58	41	44	36	42	31

		Detection Limits	T-1050	T-1055	T-1100	T-1115-8	T-1120-3	P-3-1100	P-12-1100	RA2-3-1115	RA2-12-1115
<b>Total Metals (ug/L)</b>											
Arsenic	5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Cadmium	1		ND	ND	ND	ND	ND	ND	ND	2	ND
Chromium	5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	5		44	21	12	14	9	56	16	39	17
Lead	3		ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel	10		ND	ND	ND	ND	ND	ND	ND	ND	28
Mercury	0.5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Silver	1.5		ND	ND	ND	ND	ND	ND	ND	ND	ND
Zinc	10		37	25	28	43	28	77	46	91	33
<b>Dissolved Metals (ug/L)</b>											
Arsenic	5		ND	ND	ND	ND		ND	ND	ND	ND
Cadmium			ND	ND	ND	ND		ND	ND	ND	ND
Chromium	5		ND	ND	ND	ND		ND	ND	ND	ND
Copper	5		42	17	12	8		29	14	38	16
Lead	3		ND	ND	ND	ND		ND	ND	ND	ND
Nickel	10		ND	ND	ND	ND		ND	ND	ND	24
Mercury	0.5		ND	ND	ND	ND		ND	ND	ND	ND
Silver	1.5		ND	ND	ND	ND		ND	ND	ND	ND
Zinc	10		27	26	22	ND		44	25	90	17

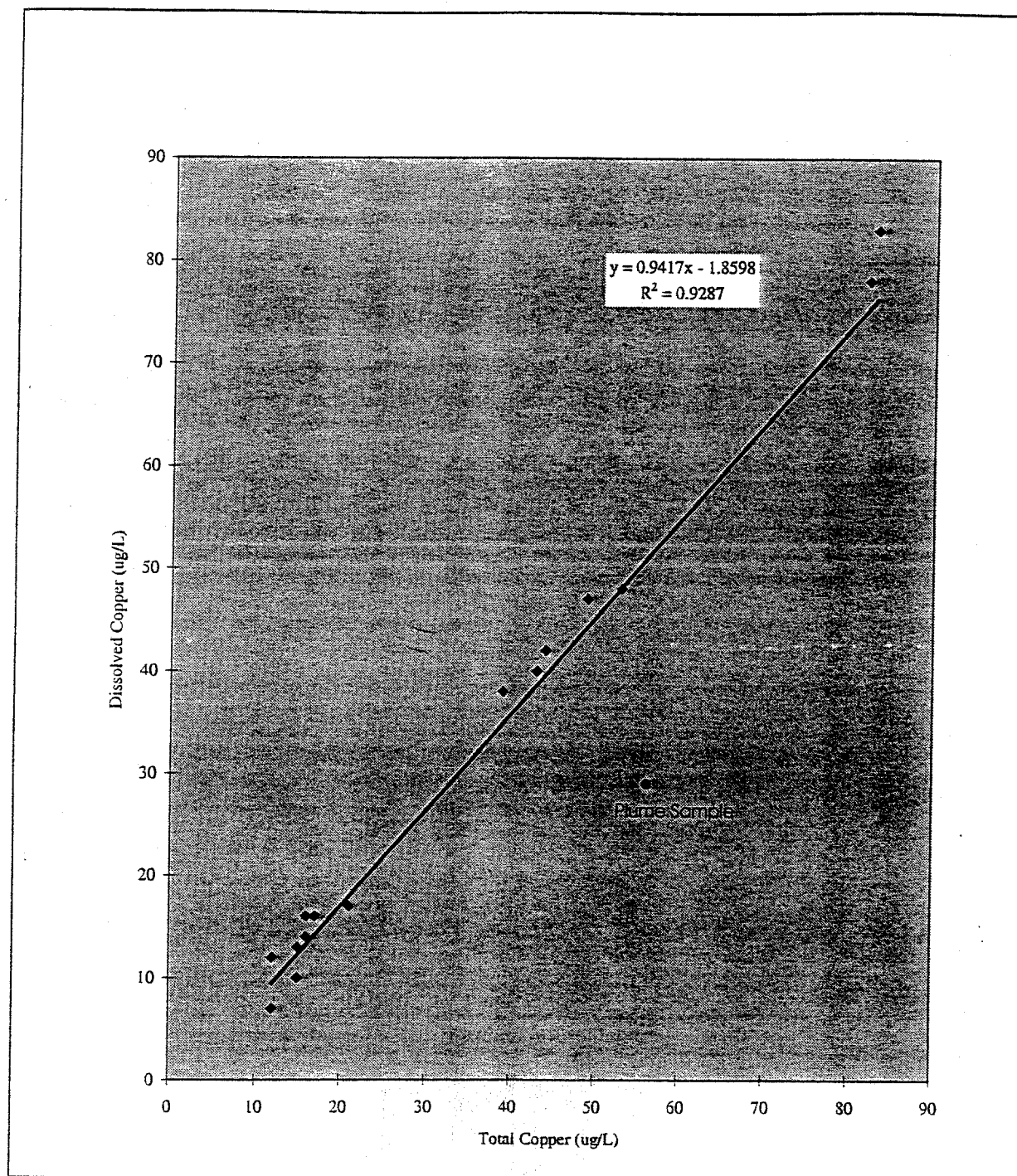


Figure 3: Total Copper vs. Dissolved Copper in Samples Collected in the Underwater Hull Cleaning Study



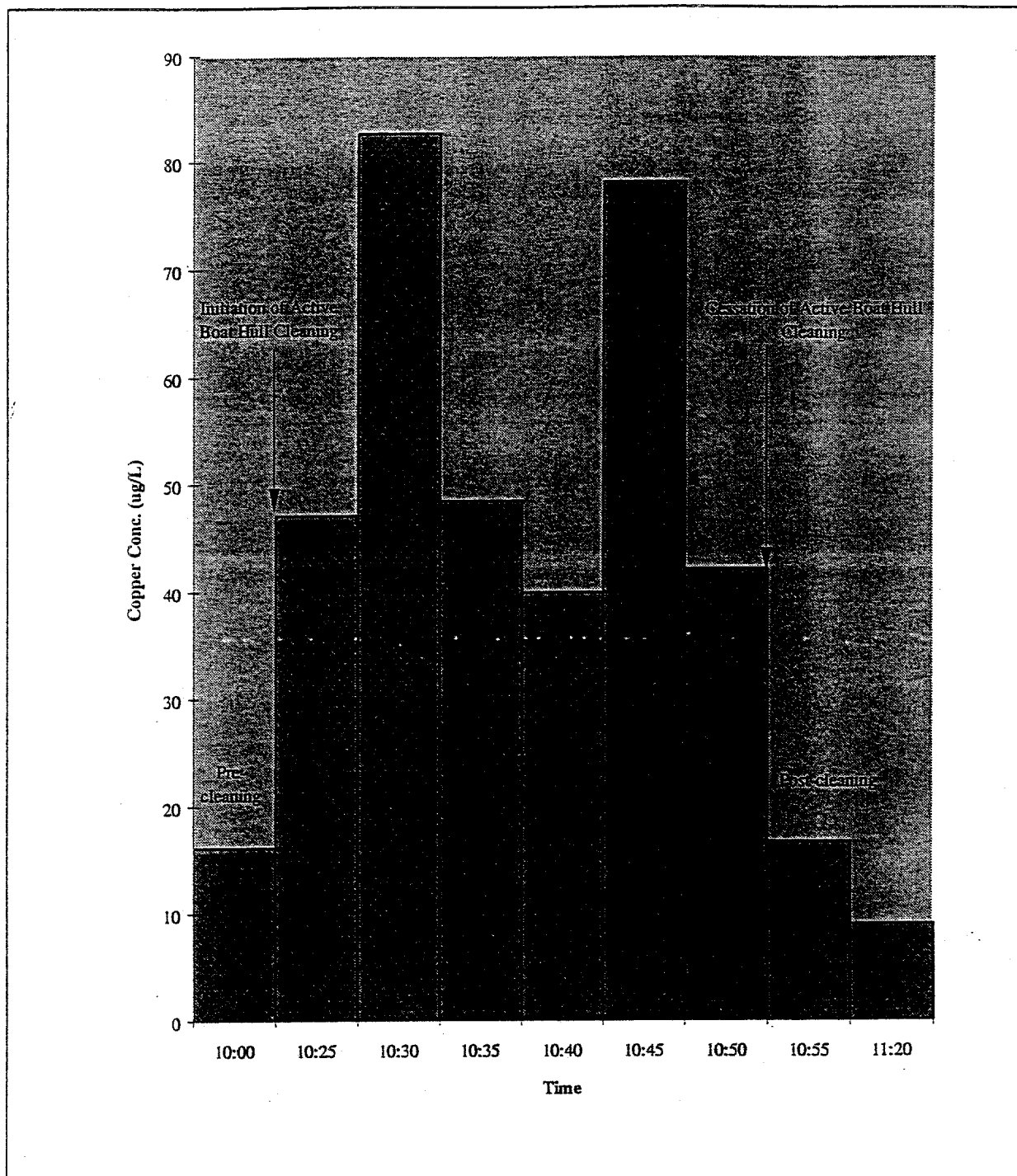


Figure 4: Dissolved Copper Concentrations before, during, and after an Underwater Hull Cleaning Operation

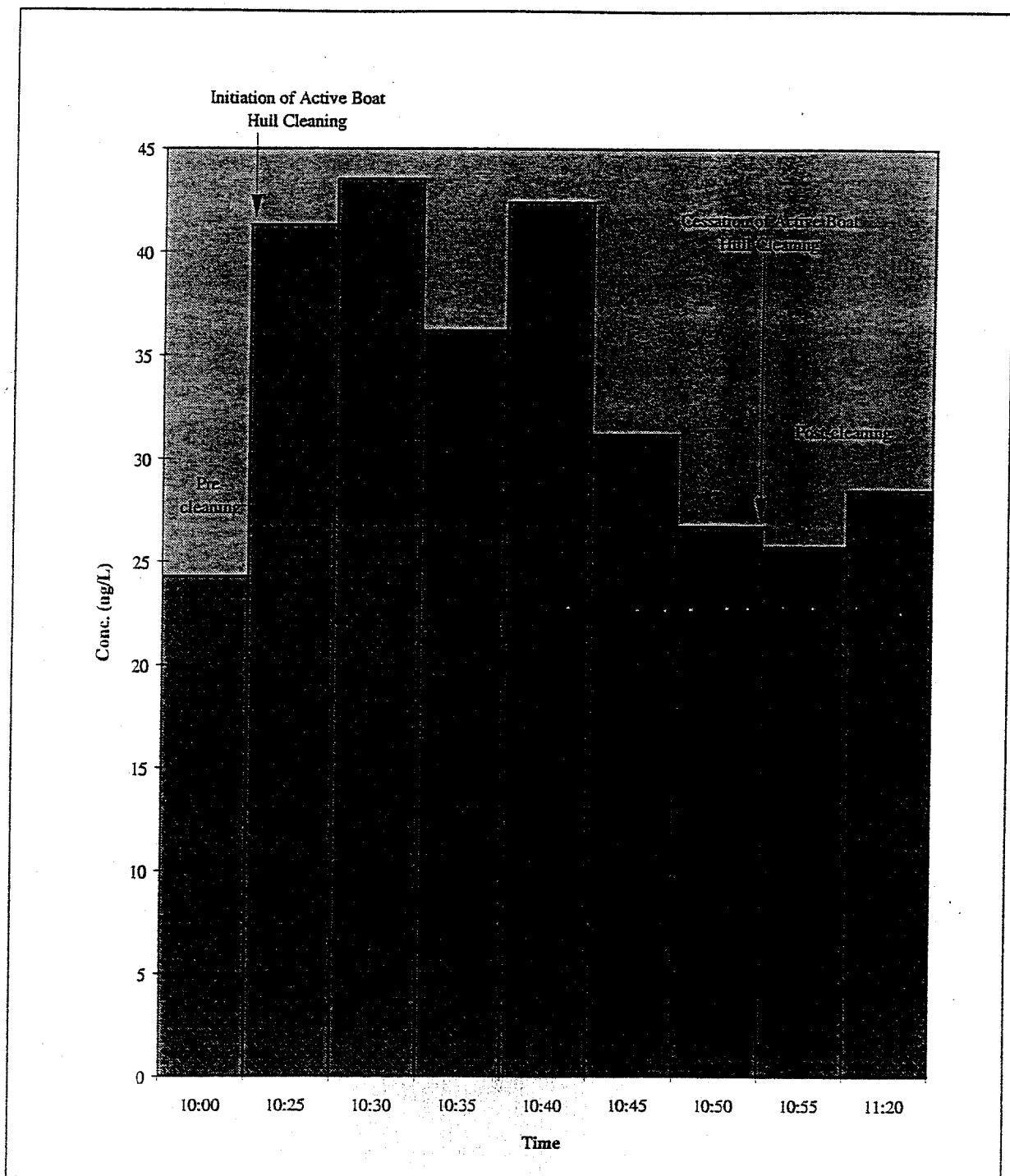


Figure 5: Dissolved Zinc Concentrations before, during, and after an Underwater Hull Cleaning Operation

### Contaminant Plume

The contaminant plume was carried by the current to the southeast and south. Since the reference site was two piers southeast of the boat cleaning operation, it may have been impacted by the plume. Samples that were taken at the reference site after the hull cleaning was completed contained copper concentrations indicative of the contaminant plume. Samples that were taken from the plume site and the reference site at a depth of 3' had copper concentrations of 29 ug/L and 39 ug/L, respectively (Fig. 6). Samples that were taken at a depth of 12' from these same two sites had dissolved copper concentrations similar to background concentrations.

### Toxicity Analysis

The toxicity of the samples collected during the hull cleaning study was determined by bioassays using the Pacific Oyster, *Crassostrea gigas* (Bivalve bioassay). Bivalves were chosen as the test organism because the U.S.EPA Ambient Water Quality Criteria for copper indicates that bivalves are some of the most sensitive saltwater animals to copper. Bivalve larvae were selected because the literature indicates that this is the most sensitive life stage of bivalves (Calabrese *et al*, 1977). The bivalve larvae bioassay generates information on both the lethal and sublethal effects of the materials tested. Lethality was measured by determining percent mortality, while sublethal effects were measured by determining the percentage of the larvae which exhibited abnormal development.

### Test Procedures

All bioassays were performed by Ogden Environmental and Energy Services, San Diego, California. Samples were tested at pre-specified dilutions, and each dilution was tested in quadruplicate. In each test, ten milliliters of each dilution was inoculated with a one milliliter aliquot from a larval solution. The larval solution consisted of one liter of clean seawater containing approximately 250,000 bivalve larvae. The test assumed that the larvae were evenly distributed as 250 larvae per milliliter. The control for this test was four vials containing a ten milliliters of filtered, UV-sterilized seawater which had been inoculated with one milliliter of the bivalve larvae solution. Following the termination of the test, the number

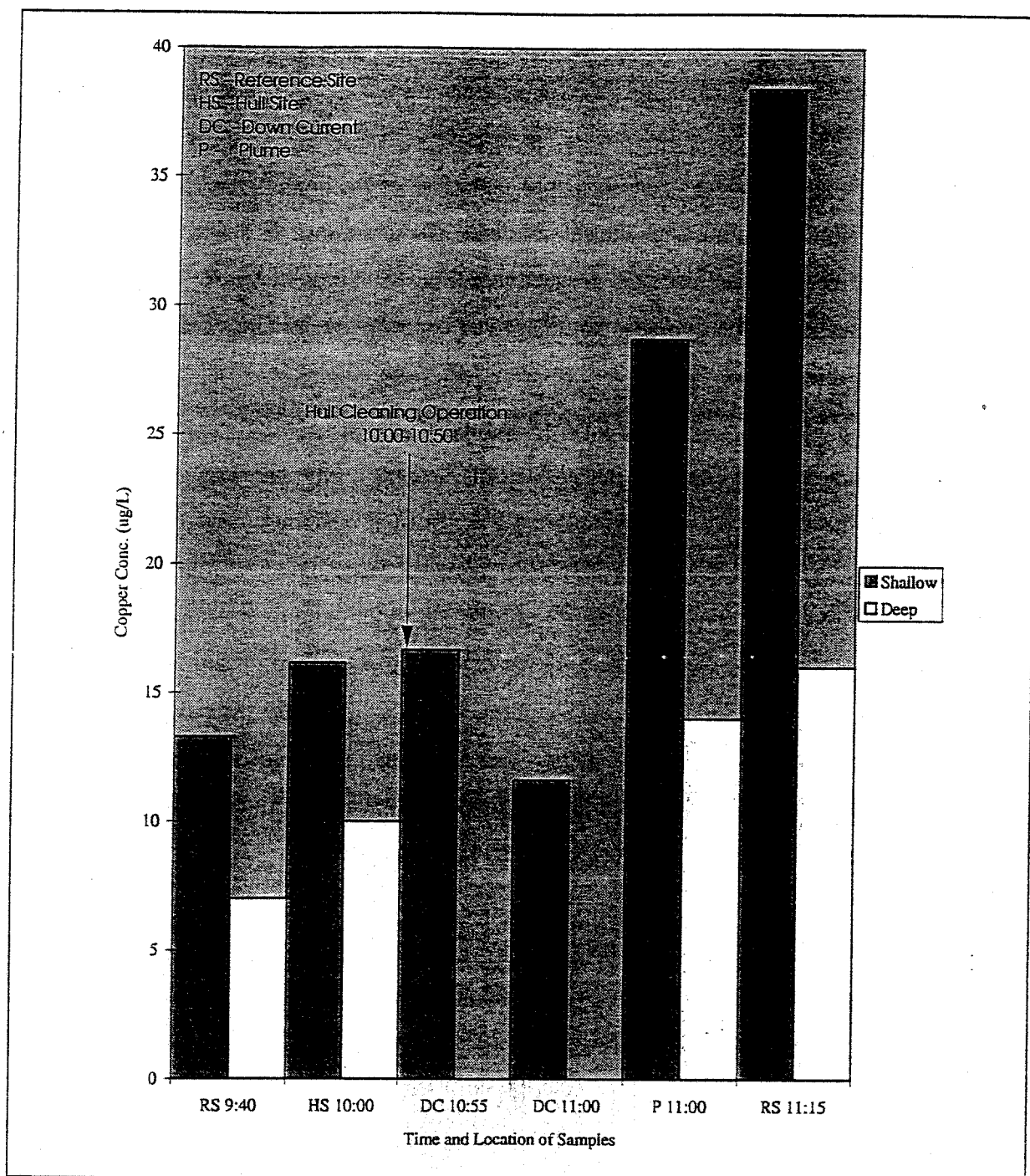


Figure 6: Copper Concentrations in Plume and Reference Samples from the Underwater Hull Cleaning Study

of surviving larvae in each vial were counted, as were the number of normal and abnormal larvae. Percent normality was determined by comparing the number of normal larvae in each vial to the total number of larvae in the vial. Percent survival was determined by dividing the mean number of viable larvae at each dilution by the mean number of viable larvae in the control sample. As such, percent survival data was based on the assumption that the one milliliter aliquots taken from the initial larval solution consistently contained 250 larvae. Results for both the survival and normality were analyzed statistically using Dunnett's procedure. Determination of survival within the control and each sample dilution was based on the assumption that each vial contained equivalent initial concentrations of larvae. Reliance on this assumption weakened the usefulness of the survival data generated by this test.

## **Bioassay Results**

### **Survival**

Several samples that were taken during the active hull cleaning operation had statistically significant reductions in survival relative to the control. Even though these samples indicate impacts on larval survival, several samples had poor dose-response relationships, thereby limiting any inferences that can be made regarding the survival impacts from the hull cleaning procedure. As previously noted, the survival data from the bivalve bioassay are also suspect due to the assumption of equivalent initial larval concentrations. The majority of the samples seem to have an improved survival response relative to the controls, while other samples with similar concentrations of dissolved copper and zinc produced a decrease in survival relative to the controls. The most likely explanation for this contradiction is a relatively high variability in the initial larval density in the test containers.

The bivalve bioassays indicate that the No Observed Effects Concentration (NOEC) for survival was approximately 20 ug/L (Fig. 7), and that at dissolved copper concentrations greater than 28 ug/L (Fig. 8), percent mortality should be expected to increase to greater

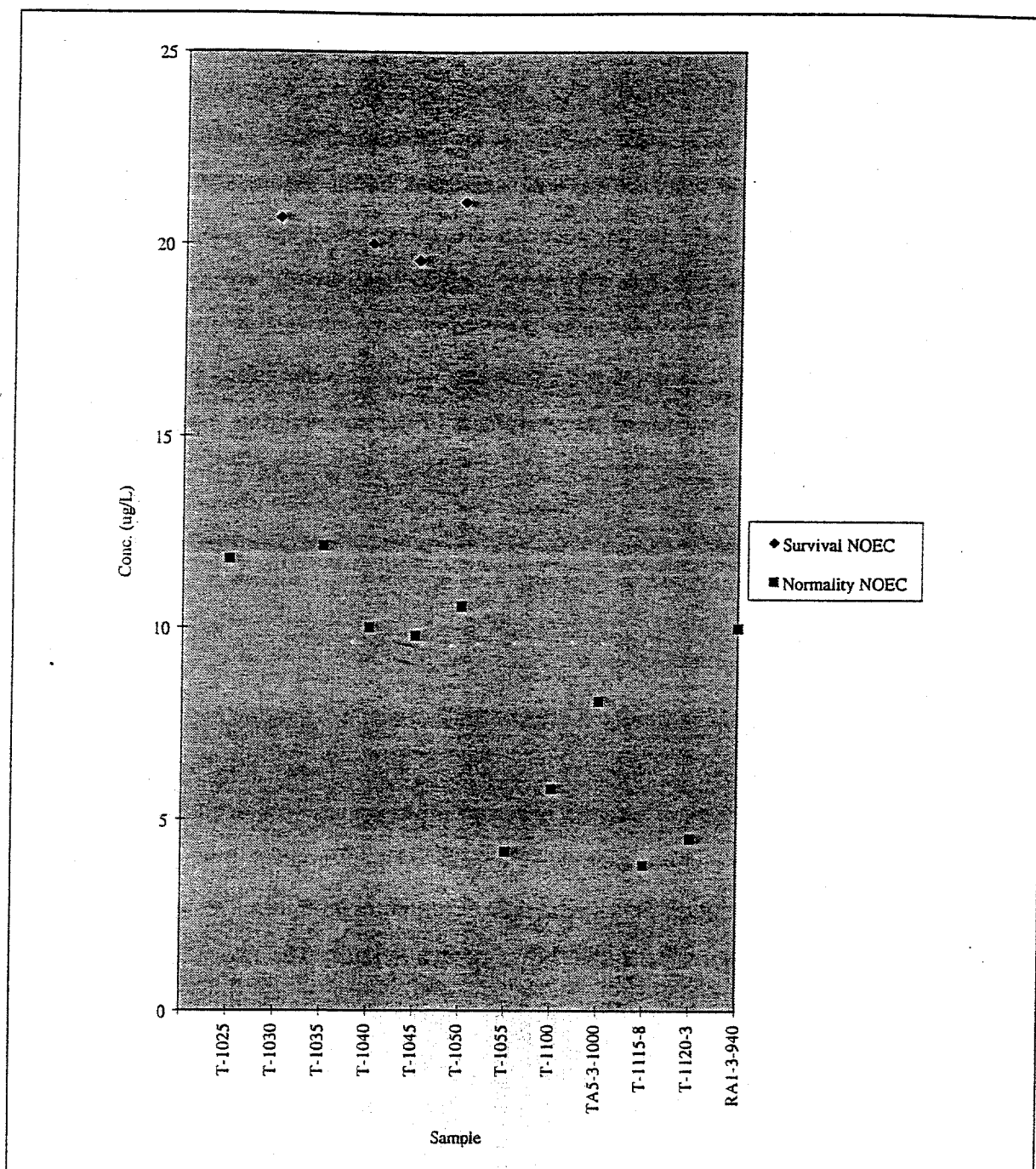


Figure 7: Dissolved Copper NOECs for Survival and Normality in the Underwater Hull Cleaning Study

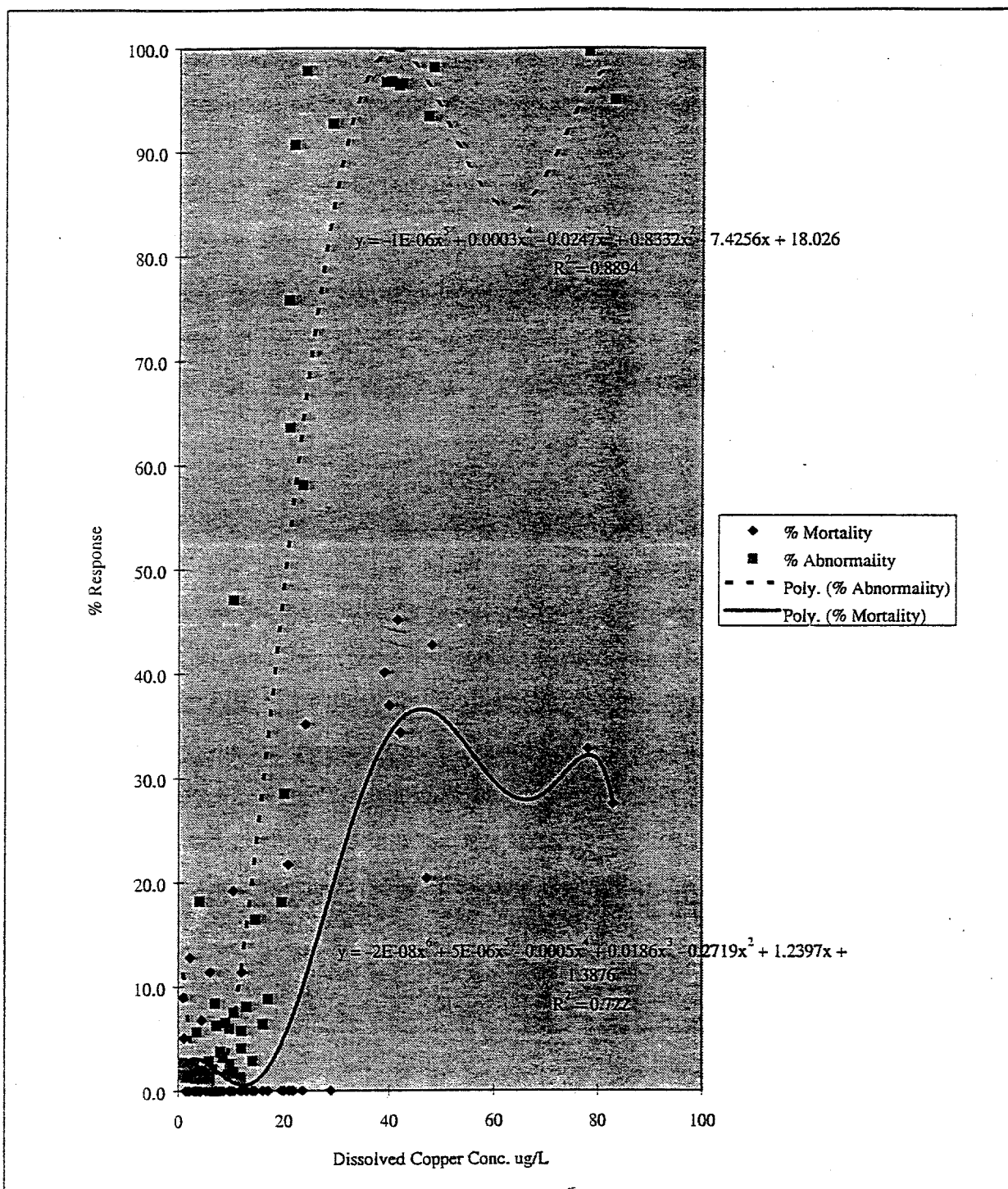


Figure 8: Copper Dose Response in Underwater Hull Cleaning Study

than 20%. Figure 8 also contains polynomial best fit lines which were generated from a regression analysis of the survival and normality data. These lines help to elucidate what appears to be a sigmoidal dose response relationship, but are not intended to imply that the dose response curve is best described by an upper order polynomial equation.

When mortality percent response is plotted against dissolved zinc concentrations, there is no apparent relationship (Fig. 9). The mortality effects which were noted were most likely due to the high dissolved copper concentrations in the samples, not the zinc. Dissolved zinc concentrations prior to, during, and after the cleaning never exceeded the U.S.EPA's Ambient Water Quality Criteria (saltwater) of 95 ug/L.

#### **Normality**

Statistically significant normality effects were present in every sample tested. The bioassays indicated that the dissolved copper NOEC for normality was approximately 5 ug/L (Fig. 7), and there was a dramatic increase in the percentage of abnormalities in the samples which were taken during the cleaning operation. At concentrations greater than 16 ug/L the number of abnormalities were very high, and at concentrations greater than 25 ug/L nearly all of bivalve larvae had abnormalities (Fig. 8). When normality percent response is plotted against dissolved zinc concentrations, there is no apparent relationship (Fig. 9). As found in the survival effects, any apparent normality effects associated with dissolved zinc concentrations were most likely due to concomitantly high dissolved copper concentrations.



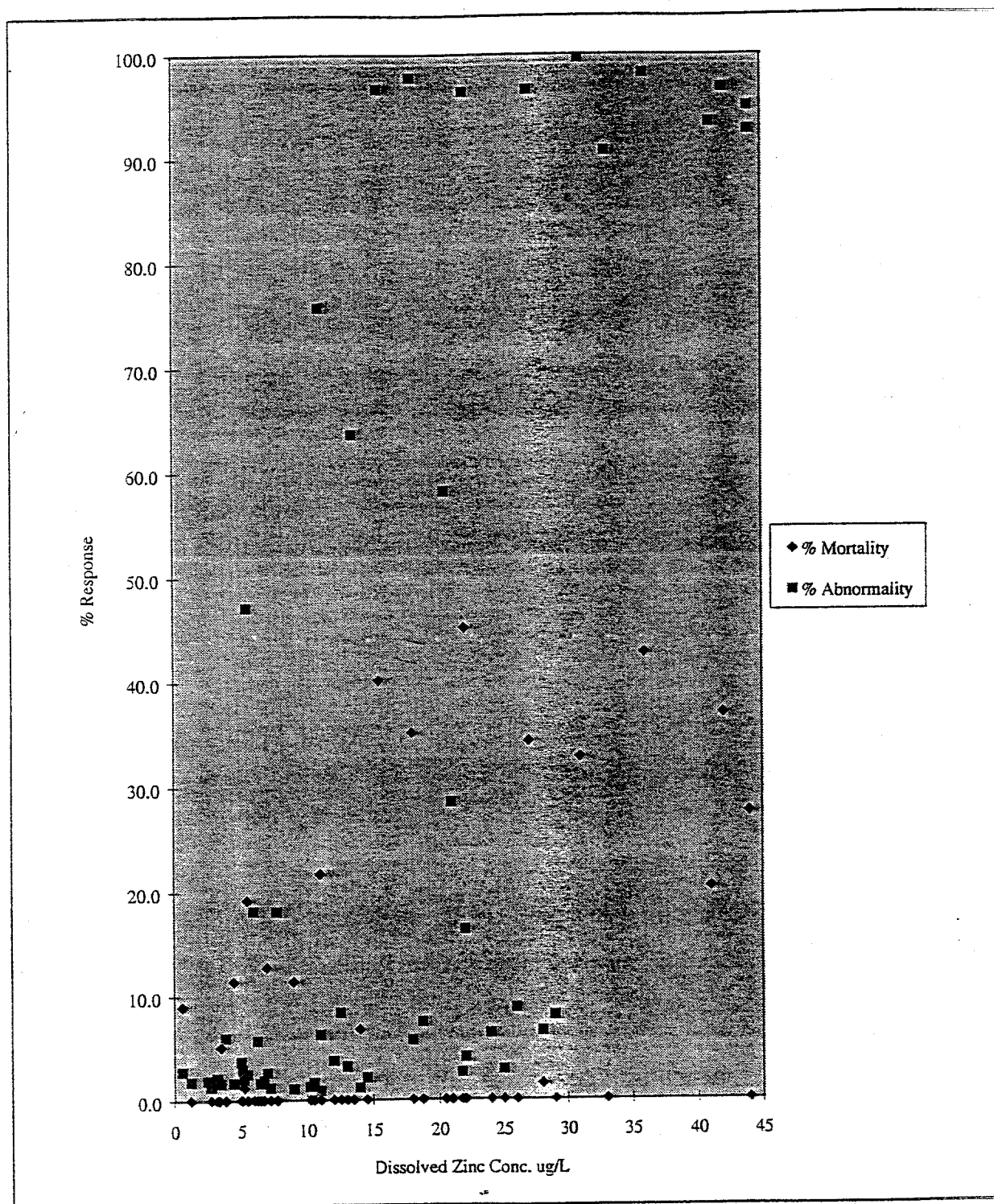


Figure 9: Zinc Dose Response in the Underwater Hull Cleaning Study



### CHAPTER III

## AMBIENT CONCENTRATIONS STUDY

In June of 1994, a study was conducted of ambient copper concentrations in regions of San Diego Bay and Mission Bay where recreational boats are harbored. Samples were taken from San Diego Bay on two occasions: June 14, 1994 and June 28, 1994. Samples were collected from Mission Bay on June 29, 1994.

### Sampling Sites

On June 14th, samples were taken from six separate regions within San Diego Bay: the Shelter Island Yacht Harbor (SI), America's Cup Yacht Harbor (AC), the East Basin (EB) and West Basin (WB) of Harbor Island, the area outside the launch ramp at Shelter Island (LR), and the area of the moored boats near Laurel Street (LS)(east of the Coast Guard Station). On June 28th, samples were taken from Glorietta Bay (GB), Intercontinental Harbor (IC), the Marina at the G-street pier (GS), the moorings just north of the Coronado Bridge (CB), and 3 stations in Shelter Island Yacht Basin were repeated (Fig. 10). Samples were collected from three regions in Mission Bay on June 29th, 1994: Quivira Basin (QB), Dana Landing (DL), and Perez Cove (PC).

All samples were intentionally taken during low tide, when ambient concentrations were expected to be the greatest. On June 14th, the low tide was 0.1 ft at 7:34 a.m. Samples were collected from 7:00 a.m. to 9:30 a.m. On June 28th, low tide was 0.3 ft at 7:45 a.m. and samples were collected from 7:47 a.m. to 10:05 a.m. On June 29th, low tide was 0.8 ft at 8:27 a.m. and samples were collected from 8:30 a.m. to 9:35 a.m.

### Analyses

Samples were analyzed by Truesdail Laboratories for total and dissolved copper and zinc, using graphite furnace atomic absorption with MIBK extraction. For the purpose of this and all other statistical analyses, all sample results that were below the limit of detection of

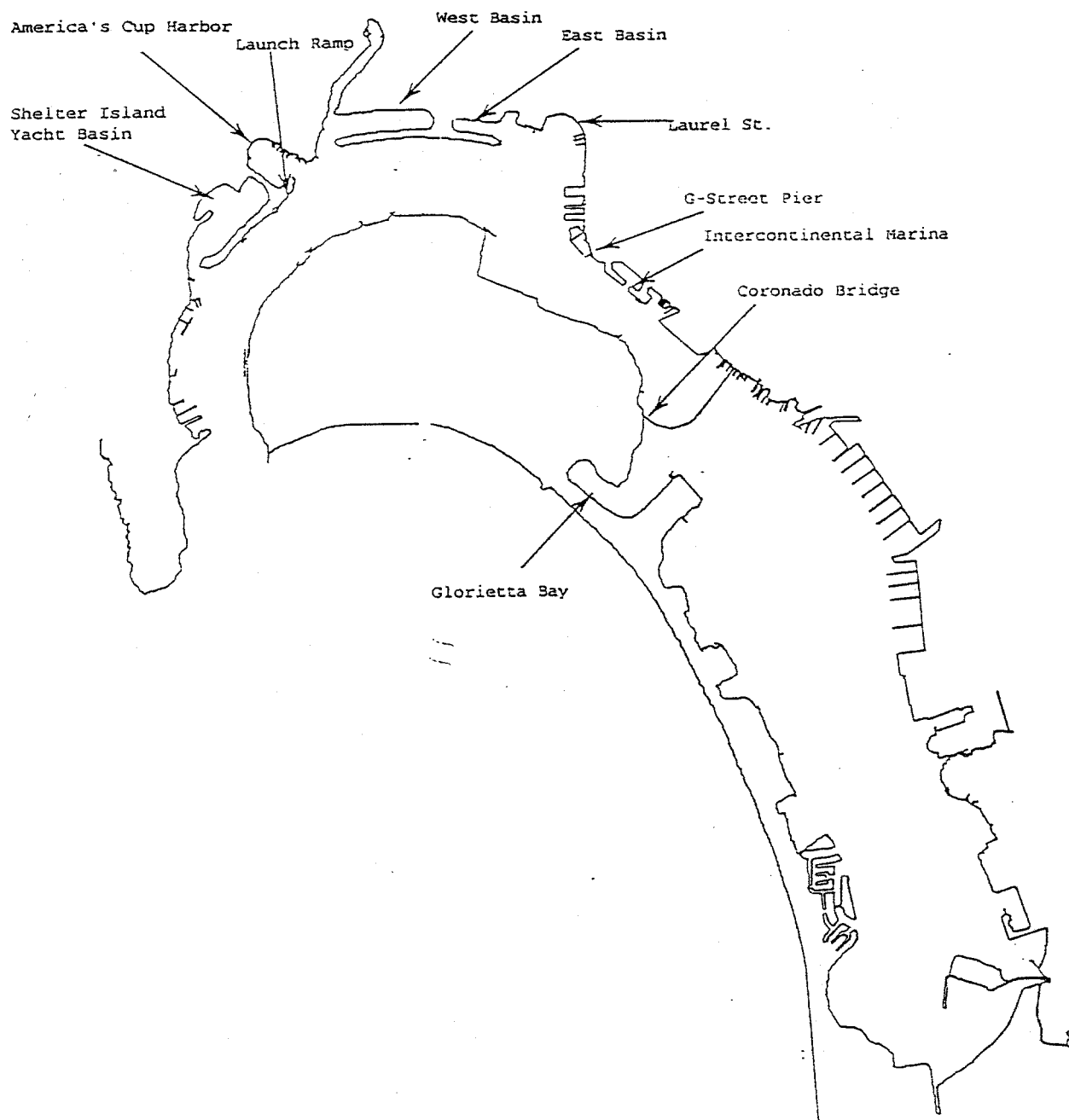


Figure 10: Regions of San Diego Bay Sampled in the Ambient Concentrations Study

5 ug/L were considered to be 2.5 ug/L. Such an assumption is supported by historical data which indicates that copper concentrations are greater in the yacht harbors of San Diego Bay than in the main channel, and that average concentrations in the main channel are approximately 3 ug/L (Zirino et al, 1978; Kenis et al, 1978; Johnston, 1990). Data from this study was analyzed using the statistical analysis toolpak of Microsoft Excel 5.0. All statistical tests were conducted with a p-value of 0.05. Ogden Environmental and Energy Services analyzed a portion of the ambient samples for chronic toxicity, utilizing larvae of the Pacific Oyster, *Crassostrea gigas* (Bivalve bioassay). The procedures used in these bioassays are described in detail within the Hull Cleaning Study section of this report.

## Results

The average concentrations of total and dissolved copper found in the San Diego Bay marinas sampled on June 14th are listed in Table II. There were no significant differences in dissolved copper concentrations between any of the regions sampled on this date. While several harbors had significantly greater total copper concentrations than the other harbors, there was no discernible trend among the harbors or any discernible gradient of concentration within each harbor.

The average copper concentrations found in the San Diego Bay marinas sampled on the June 28th are listed in Table III. There were no statistically significant differences in total or dissolved copper concentrations between any of the harbors tested. Although dissolved copper concentrations were equivalent among the marinas tested on each date (June 14th and June 28th), there were differences found between the two dates. Dissolved copper concentrations measured in samples collected from Shelter Island Yacht Harbor on June 14th were significantly greater (at a p-value of 0.05) than the concentrations measured in the samples collected on June 28th from the same harbor locations. The differences in the dissolved copper concentrations between the two dates may be partially due to sampling variability, but may also be due to differences in tidal flushing and activities within the marina during the days which preceded each sampling date.

Table II: Copper Concentrations (ug/L) in San Diego Bay Marinas on June 14, 1994

Constituent	SI	AC	EB	WB	LS	LR
<b>Total Cu</b>						
Range	2.5-8	2.5-11	7-10	5-7	2.5	2.5
Mean	5.8	3.7	8.2	7.2	2.5	2.5
Median	6.0	2.5	8.0	7.5	2.5	2.5
n	14	12	6	10	3	2
Std. Dev.	2.0	2.6	1.0	1.3	0.0	0.0
<b>Dissolved Cu</b>						
Range	2.5-7	2.5-6	2.5-10	2.5	2.5	2.5
Mean	4.1	2.8	5.1	2.5	2.5	2.5
Median	2.5	2.5	2.5	2.5	2.5	2.5
n	14	12	5	9	3	2
Std. Dev.	2.1	1.0	3.6	0.0	0.0	0.0

Table III: Copper Concentrations (ug/L) in San Diego Bay Marinas on June 28, 1994

Constituent	SI	GS	IC	GB	CB
<b>Total Cu</b>					
Range	2.5	2.5	5-26	2.5-14	2.5
Mean	2.5	2.5	8.3	3.8	2.5
Median	2.5	2.5	6.0	2.5	2.5
n	3	4	9	9	2
Std. Dev.	0.0	0.0	6.7	3.8	0.0
<b>Dissolved Cu</b>					
Range	2.5	2.5	2.5-6	2.5	2.5
Average	2.5	2.5	2.9	2.5	2.5
Median	2.5	2.5	2.5	2.5	2.5
n	3	4	9	9	2
Std. Dev.	0.0	0.0	1.2	0.0	0.0

The average copper concentrations found in the Mission Bay marinas sampled on June 29th are listed in Table IV. There were no significant differences in total or dissolved copper concentrations between any of the harbors tested.

The average concentrations of total and dissolved copper found in San Diego and Mission Bays are listed in Table V. Statistical analysis of the data, utilizing the Student's paired t-test for sample means, reveals that total copper concentrations in San Diego Bay were significantly greater than dissolved copper concentrations. In Mission Bay, the Student's paired t-test for sample means indicates that there was no significant difference between the total and dissolved fractions of copper. Further analysis using the Student's t-test for sample means reveals that copper concentrations in San Diego Bay between the two sampling dates were not significantly different. When the results from the samples collected on June 28th in San Diego Bay were compared to those from samples collected on June 29th in Mission Bay, there was no apparent difference in copper concentrations.

Since dissolved copper concentrations were statistically equivalent in marinas across San Diego Bay, and between San Diego and Mission Bays, the relative toxicity expected in each marina in the two bays, (which can be attributable to copper), may also be expected to be equivalent. This appears to be the case. There was no obvious toxicity in the many bivalve bioassays which were conducted as part of the Ambient Concentrations Study. Those few samples which indicate possible toxicity, had poor replication, and other samples with similar concentrations of copper exhibited no toxicity. Any apparent toxicity in any of the tests appears to be more attributable to an aberration in the test, rather than to the presence of toxic conditions. While current ambient copper concentrations appear to be non-toxic, (according to the results of the bivalve bioassays), several marinas did have average dissolved copper concentrations that were above the U.S. EPA's Ambient Water Quality Criteria for saltwater aquatic life.



Table IV: Copper Concentrations (ug/L) in Mission Bay Marinas on June 29, 1994

Constituent	DL	QB	PC
<b>Total Cu</b>			
Range	2.5	2.5-6	2.5
Average	2.5	2.9	2.5
Median	2.5	2.5	2.5
n	3	9	2
Std. Dev.	0.0	1.2	0.0
<b>Dissolved Cu</b>			
Range	2.5	2.5-5	2.5
Average	2.5	2.8	2.5
Median	2.5	2.5	2.5
n	3	9	2
Std. Dev.	0.0	0.8	0.0

Table V: Average Copper Concentrations (ug/L) in San Diego (SD) and Mission Bays (MB)

Constituent	SD Bay 6/14	SD Bay 6/28	MB 6/29
<b>Total Cu</b>			
Range	2.5-10	2.5-26	2.5-6
Mean	5.5	4.9	2.8
Median	6.0	2.5	2.5
n	46	27	14
Std. Dev.	2.6	5.0	0.9
<b>Dissolved Cu</b>			
Range	2.5-10	2.5-6	2.5-5
Mean	3.4	2.6	2.7
Median	2.5	2.5	2.5
n	46	27	14
Std. Dev.	1.9	0.7	0.7

## CHAPTER IV

### TIDAL INFLUENCE STUDY

The effects of the tidal cycle on dissolved copper and zinc concentrations in recreational boat harbors was evaluated by sampling at the initiation of a the tidal cycle, and then once per hour thereafter until the start of the next tidal cycle. The study was initiated at 0630 on June 14, 1994 and ended at 1830 on that same date. The low tides and high tides associated with this study are listed in Table VI. At each sampling time, samples were taken from the surface, 3 feet from the surface, and 9 feet from the surface using a Niskin bottle. Samples were collected from the end of a pier in the Bay Club Marina in the Shelter Island Yacht Harbor of San Diego Bay. This was also a site used in the Ambient Concentrations Study.

Table VI: Tide Table, June 14, 1994

Tide	Time	Height (ft)
High	0018	4.8
Low	0734	0.1
High	1433	4.1
Low	1945	2.5

### Results

Fluctuations in dissolved copper concentrations throughout the tidal cycle are listed in Table VII. For the purpose of statistical analysis all sample results that were below the limit of detection of 5 ug/L were considered to be 2.5 ug/L. Data from this study were analyzed using the statistical analysis toolpak of Microsoft Excel 5.0. All statistical tests were

conducted with a p-value of 0.05. The water column average is the average of the copper concentrations across the three depths sampled at a specific time.

Table VII: Hourly Dissolved Copper Concentrations (ug/L)

Time	Shallow	3' Deep	9' Deep	Water Column Avg.	Std. Dev.
0630	11	12	12	11.7	0.6
0730	12	12	9	11.0	1.7
0830	8	9	2.5	6.5	3.5
0930	11	11	7	9.7	2.3
1030	10	9	9	9.3	0.6
1130	9	5	5	6.3	2.3
1230	8	9	9	8.7	0.6
1330	11	6	2.5	6.5	4.3
1430	6	7	7	6.7	0.6
1530	5	7	2.5	4.8	2.3
1630	6	6	6	6.0	0.0
1730	8	6	2.5	5.5	2.8
1830	6	2.5	8	5.5	2.8

A regression analysis of the copper data versus time (Fig. 11) indicates that copper concentrations were weakly correlated with time. When the temporal fluctuations in dissolved copper concentrations are graphically compared with the tidal cycle, there is no apparent relationship (Fig. 12). Such a conclusion is supported by an analysis of variance of the water column averages which indicates that concentrations in the samples collected from

0730 to 1830 were not significantly different. The positive correlation between copper concentrations throughout the water column - (i.e. high concentrations in the shallow water accompanied by high concentrations in deeper water at the same sampling time) - indicates that throughout the tidal cycle a fluctuation in the copper concentration of one portion of the water column is accompanied by similar fluctuations in the remainder of the water column.

Fluctuations in dissolved zinc concentrations throughout the tidal cycle are listed in Table VIII. A regression analysis of the zinc data versus time (Fig. 13) indicates that zinc concentrations are only weakly correlated with time. When the temporal fluctuations in dissolved zinc concentrations are compared with the tidal cycle (Fig. 14), there is no apparent relationship. The positive correlation between zinc concentrations in each segment of the water column indicates that during the tidal cycle a fluctuation in the zinc concentration of one portion of the water column is accompanied by similar fluctuations in the remainder of the water column. While a single factor analysis of variance (ANOVA) of the dissolved zinc data indicates that the mean hourly concentrations throughout the water column are not equivalent, the effect of the tide on dissolved zinc concentrations was apparently negligible.

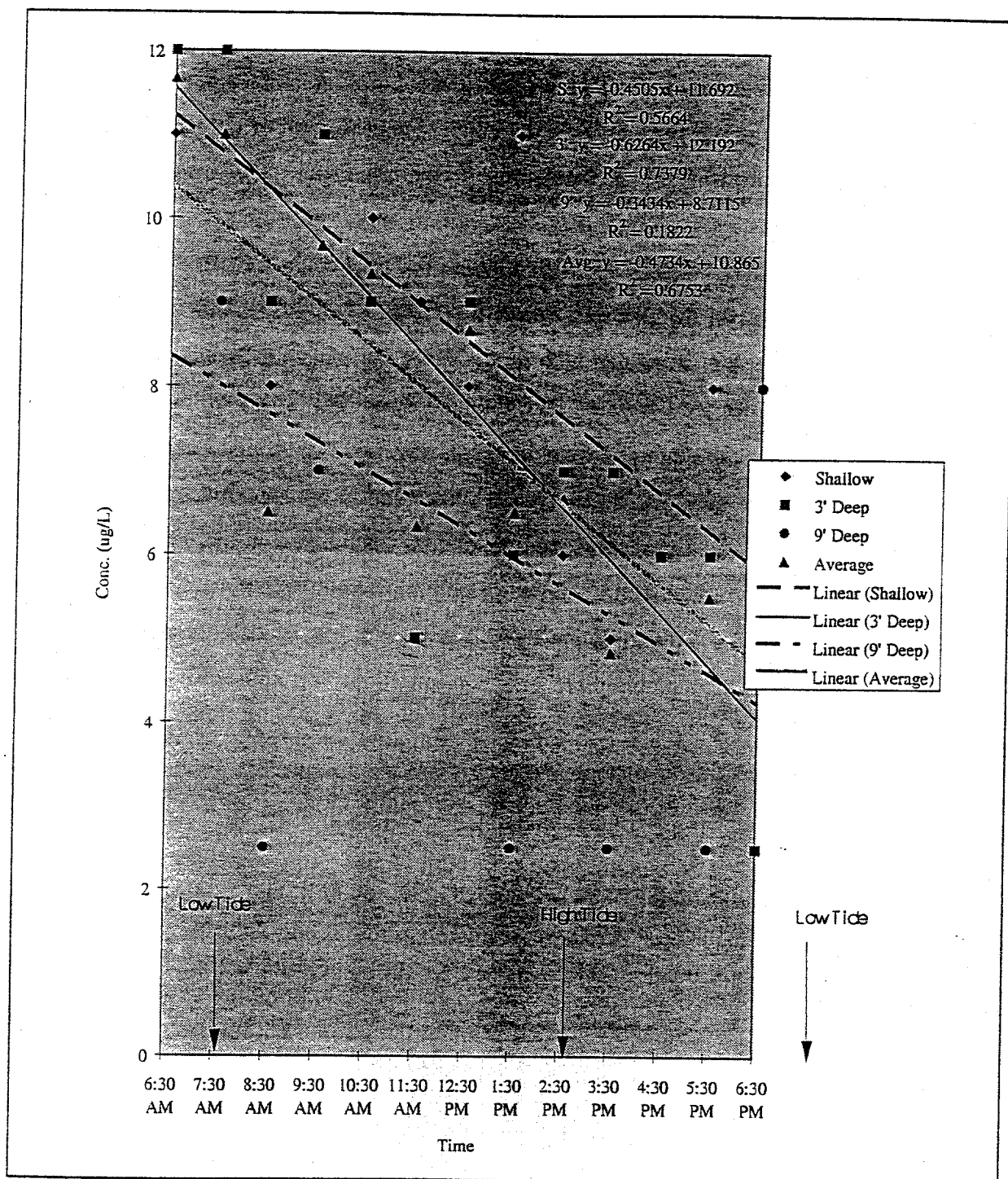


Figure 11: Regression Analysis of Dissolved Copper vs. Time

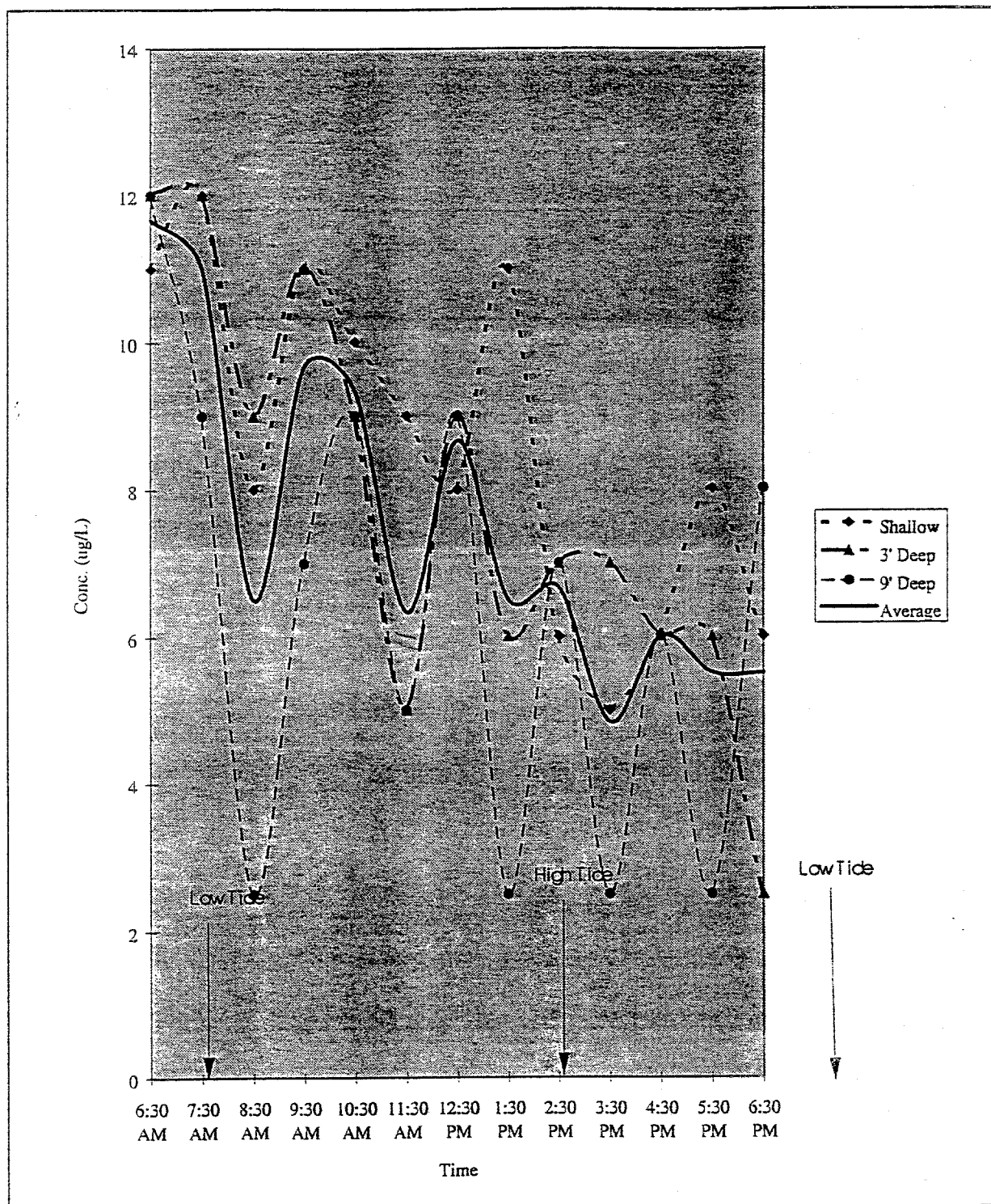


Figure 12: Dissolved Copper Concentrations vs. the Tidal Cycle

Table VIII: Hourly Dissolved Zinc Concentrations (ug/L)

Time	Shallow	3' Deep	9' Deep	Water Column Avg.	Std. Dev.
0630	7	20	16	14.3	6.7
0730	21	23	23	22.3	1.2
0830	17	19	15	17.0	2.0
0930	16	20	16	17.3	2.3
1030	17	22	31	23.3	7.1
1130	22	2.5	20	14.8	10.7
1230	61	29	28	39.3	18.8
1330	9	2.5	2.5	4.7	3.8
1430	13	29	11	17.7	9.9
1530	2.5	2.5	17	7.3	8.4
1630	2.5	2.5	2.5	2.5	0.0
1730	2.5	2.5	2.5	2.5	0.0
1830	2.5	2.5	2.5	2.5	0.0



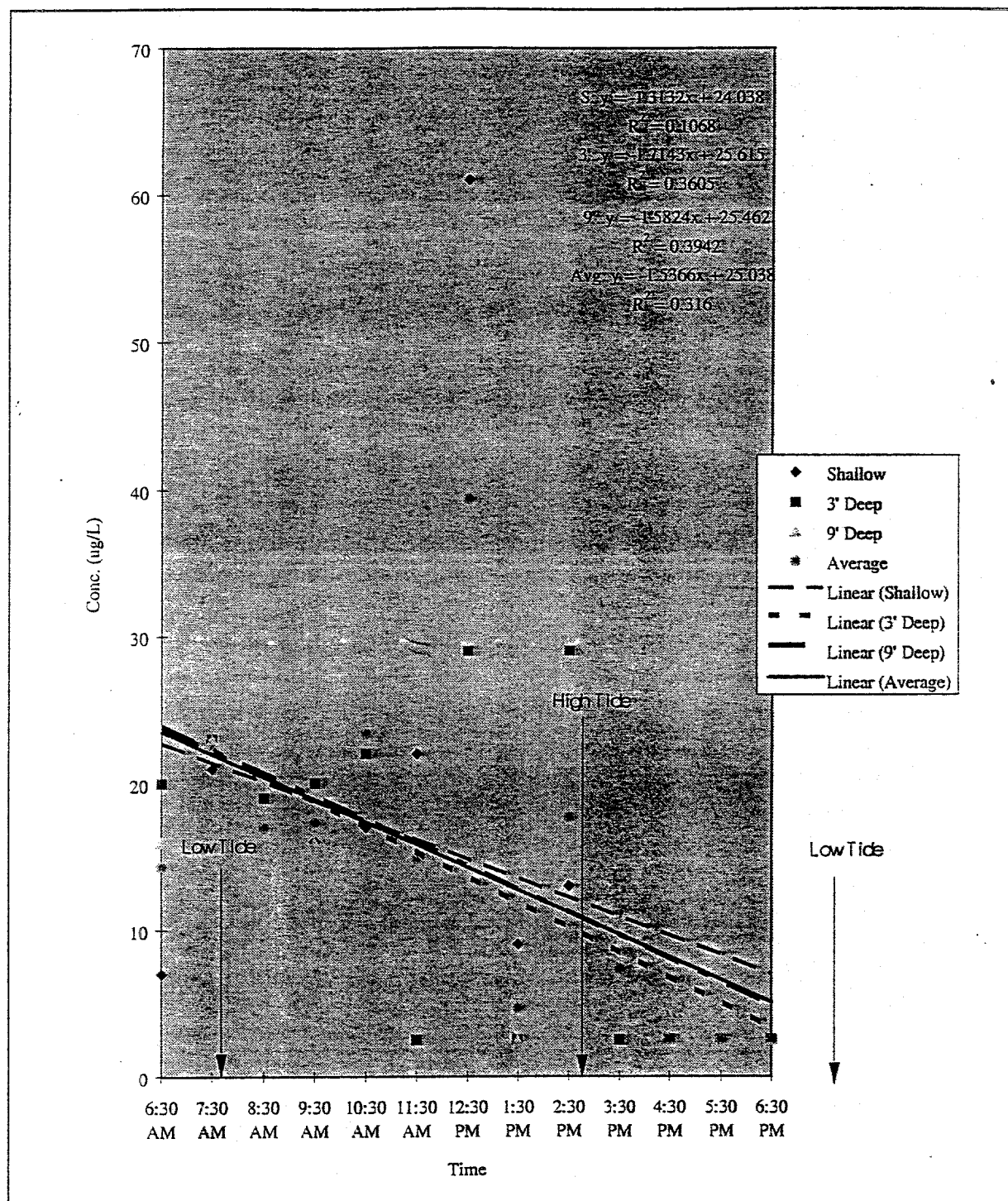


Figure 13: Regression Analysis of Dissolved Zinc vs. Time

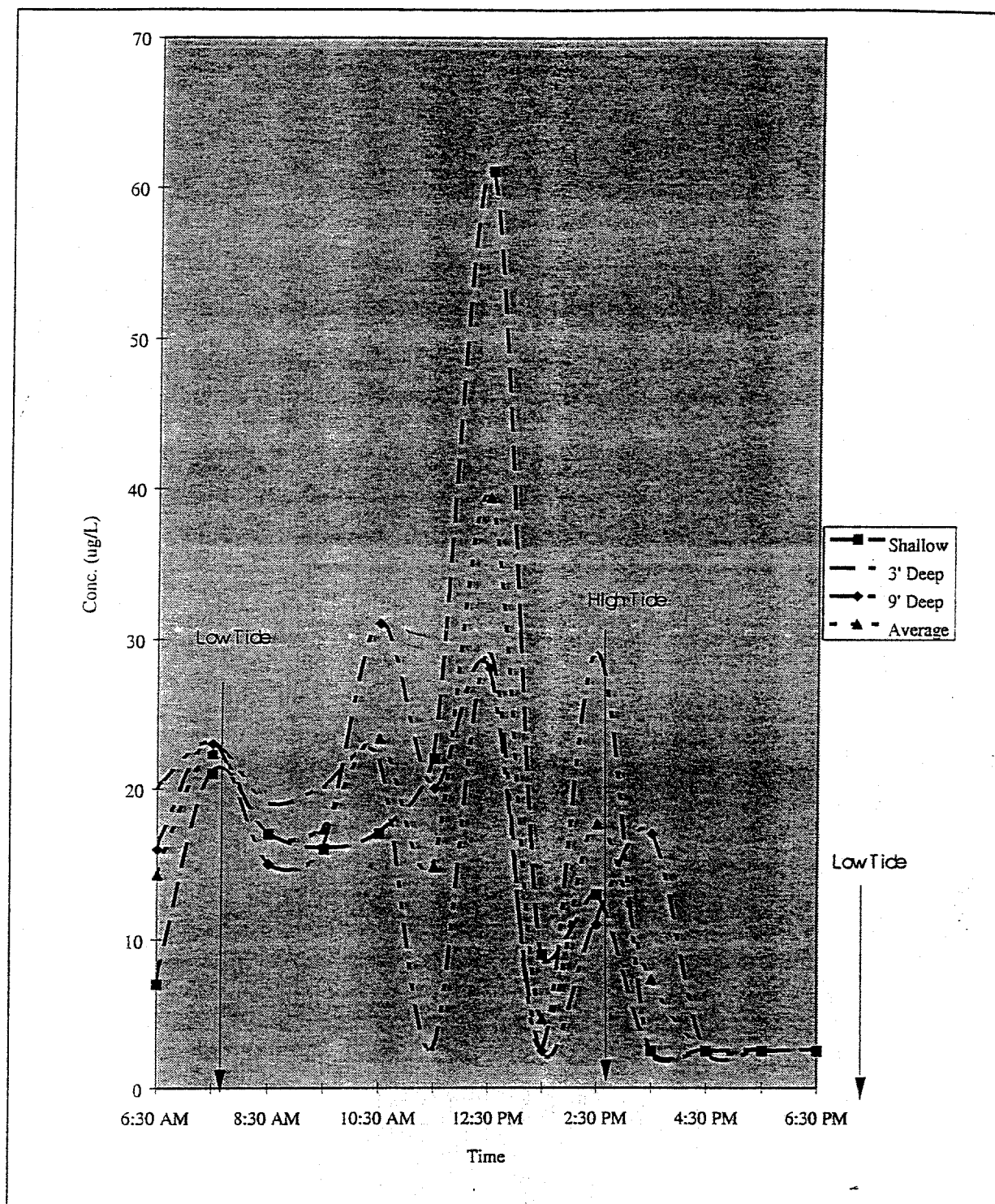


Figure 14: Dissolved Zinc vs. the Tidal Cycle

## CHAPTER V

### CONCLUSIONS

As previously stated, the purpose of the studies discussed above was to examine and elucidate the impacts that the harborage and in-water maintenance of recreational boats is having on the water quality and marine habitat beneficial uses of San Diego and Mission Bays. These studies were designed to: (1) estimate the impact underwater hull cleaning operations have on copper concentrations, (2) estimate the toxicity associated with underwater hull cleaning operations, (3) determine ambient copper concentrations in the yacht harbors of San Diego and Mission Bay, (4) determine if there is any toxicity resulting from the ambient conditions in the yacht harbors, and (5) evaluate the effect of the tidal cycle on ambient copper concentrations in a San Diego Bay yacht harbor. The conclusions which can be reached from these studies are discussed below.

#### Underwater Hull Cleaning

Based on the findings of the Underwater Hull Cleaning Study, once a hull cleaning operation is initiated dissolved copper concentrations may be expected to increase rapidly, reaching concentrations that are significantly greater than the U.S.EPA Ambient Water Quality Criteria for the protection of saltwater aquatic life. At the end of a hull cleaning, the water in the vicinity of the boat can be expected to rapidly return to pre-cleaning concentrations, and the water having an elevated dissolved copper concentration will move in a contaminant plume with the current. Because the boat used in the Underwater Hull Cleaning Study was relatively clean and the diver conducting the operation was using only a moderately abrasive pad (which is commonly considered to be a best management practice), that study may underestimate the release of copper from less environmentally sensitive cleaning practices. The cleaning of more heavily fouled boats, using more rigorous removal techniques, could result in the release of substantially greater concentrations and quantities of copper to the surrounding environment.

In contrast, the actual impact to bay waters from a hull cleaning operation would not be expected to be as great as that exhibited in the bioassays which were performed in the hull cleaning study. While chronic toxicity tests are clearly appropriate for an evaluation of ambient conditions, (where long term exposure can be assumed), they are less appropriate for an evaluation of the effects of underwater hull cleaning. The hull cleaning samples were collected from within the contaminant plume as it came off the boat, and thus the samples discount the effects of dilution and dispersion. For the results of the hull cleaning bioassays to be directly applicable to bay waters, the plume resulting from a hull cleaning operation would have to remain intact and the organisms would have to be in constant exposure to the plume for 48 hours (the duration of the bioassays). This is an unrealistic expectation, given that four complete tidal cycles will occur during any 48 hour period.

The extent and degree of dispersal of the contaminant plume, and the total load to the Bay from a hull cleaning operation are difficult to infer from the data collected in the Underwater Hull Cleaning Study. In a study of the impacts of underwater hull cleaning of Naval vessels, Valkirs *et al* followed and tested hull cleaning contaminant plumes for cupric ion activity. In that study, cupric ion activity was elevated in the contaminant plume, but it returned to ambient levels within a few hours. If the discharge from an underwater hull cleaning of a recreational boat is similar to that from a Naval vessel, then the toxic impact of a cleaning can be expected to be temporally and spatially limited. Using results from Young's 1979 survey of copper-containing paint application, Valkirs *et al* also calculated the current amount of copper-containing paint being applied to recreational boats in San Diego Bay and the total copper load expected from that application. Valkirs *et al* estimated that 22,000 liters of copper containing paint is applied to hulls in San Diego Bay. Assuming that all 22,000 liters of paint applied is ablative matrix paint with an average diffusion rate of  $10 \text{ ug Cu/cm}^2/\text{day}$ , the total load to the bay from recreational boats is 56 metric tons of copper per year. If underwater hull cleaning operations increase the rate of biocide release or result in an increased frequency of hull repainting, the aggregate effect of underwater hull cleaning operations may be to increase the total load to the bay. The actual magnitude and environmental consequences of such an increase in total loading is not known.

In order to more fully elucidate the impacts of an underwater hull cleaning operation on the entire marine ecosystem, more data need to be collected on: (1) the total load of copper from the procedure, (2) the extent of plume dispersal and dilution, (3) the point of deposition of the released copper, (4) the effect on biocide release rates and repainting schedules, and (5) the fate and species of copper released during the cleaning. Furthermore, efforts should be taken to improve boat owner knowledge of biofouling so that they can make sound, informed, and environmentally sensitive decisions regarding their approach to the problem of biofouling. Nichols (1988) concluded that educating boat owners about the appropriate use of antifouling paints could reduce the total load to San Diego Bay by 33%. While underwater hull cleaning should not be done so frequently that it contributes to a need for more frequent hull repainting, it should be done at frequency which will allow the use of less abrasive, more environmentally sensitive, hull cleaning techniques. If a boat hull becomes so heavily encrusted with fouling growth that it cannot be removed by the non-rigorous use of hand held carpet or scrubbing pads, the cleaning work should be done at a boatyard, not underwater by a diver.

### **Ambient Concentrations**

The Ambient Concentrations Study found that ambient concentrations of dissolved copper in the marinas of both San Diego and Mission Bays exceed U.S. EPA Ambient Water Quality Criteria for the protection of saltwater life, yet no apparent toxicity was observed in the very sensitive bivalve larvae bioassays. Although dissolved zinc was found in detectable levels in most water samples, it was never found in excess of the U.S. EPA Ambient Water Quality Criteria.

Differences in copper concentrations (total and dissolved) between the ambient study and the underwater hull cleaning study are most likely due to sampling differences. During the hull cleaning study, samples were collected in closer proximity to the boat hulls, where copper concentrations are likely to be higher. Total copper concentrations in Mission Bay were lower than those of San Diego Bay - a result which may be due to the lesser number of boats

and industries, better tidal flushing, and/or reduced levels of suspended particulates, in Mission Bay marinas. In contrast, dissolved copper concentrations were equivalent in both bays.

While several of the marinas sampled in the ambient study did have total copper concentrations that were significantly greater than those in other marinas, dissolved copper concentrations in the marinas were not significantly different on any day of testing. As found in several earlier studies, the Ambient Concentrations Study found that copper concentrations in the marinas of San Diego Bay can be expected to be significantly greater than those in the main channel of the bay.

Since dissolved copper concentrations were statistically equivalent in marinas across San Diego Bay, and between San Diego and Mission Bays, the relative toxicity expected in each marina in the two bays, (which can be attributable to copper), is also equivalent. There was no obvious toxicity in the many bivalve bioassays which were conducted as part of the Ambient Concentrations Study. While current ambient copper concentrations appear to be non-toxic, (according to the results of the bivalve bioassays), several marinas did have average dissolved copper concentrations that were above the U.S. EPA's Ambient Water Quality Criteria for saltwater aquatic life. Although Johnston (1990) found that a copper gradient in Shelter Island Yacht Harbor appeared to have contributed to a gradient in reduced species diversity, the Ambient Concentrations Study failed to find any apparent toxicity in the water column of that, or any other marinas, during the time of the sampling.

The results from the Ambient Concentrations Study are comparable to those of past studies and indicate that over the past 20 years there does not appear to be any appreciable increase in dissolved copper concentrations in the marinas of San Diego Bay. During a large portion of those 20 years many recreational boat owners used TBT-based antifouling paints, which may contribute to the lack of any increase in dissolved copper concentrations in the bay. To protect the various habitat beneficial uses of coastal waters in the region, harbors in San Diego and Mission Bays should be monitored to assure that copper concentrations are not

increasing to toxic levels. Where possible, the methods of chemical analyses used in such monitoring programs should have detection limits below the EPA aquatic life criteria and speciate the copper to more accurately estimate the degree of toxicity which can be expected.

### **Tidal Influence**

No significant differences, attributable to tidal cycle, were noted in dissolved copper or zinc concentrations in the Tidal Influence Study. Contaminant concentrations appeared to be nearly uniform throughout the water column, and concentrations had a weak negative relationship with time, which was not associated with tidal fluctuations. Using a continuous monitoring, low detection limit anodic stripping voltammetry system, Zirino *et al* (1978) and Johnston (1990) noted an influence of the tidal cycle on copper concentrations. Limitations in the study design of the Tidal Influence Study - i.e. limited frequency of sampling, poor detection limits, and no replication of samples - may be responsible for the lack of any apparent relationship between copper concentrations and the tidal cycle in this study. Future studies should utilize continuous monitoring with improved detection limits.

The Tidal Influence Study did help confirm that the time of the sampling for the Ambient Concentrations Study, (ie. during the lowest low tide of the day), was likely to obtain the highest concentrations. Samples collected during higher tidal conditions could be expected to contain somewhat lower concentrations of copper, but the large variability in the Tidal Influence Study data precludes any predictive use of the data.

### **General Conclusions**

Based on the studies summarized in this report, there appears to be no significant deleterious effects (within the water column) of recreational boat marinas, which can be attributable to the release of copper from the harborage and in-water maintenance of the recreational boats, beyond the immediate vicinity of the boat hulls. Even though the underwater hull cleaning study indicates that copper releases can be significant in the immediate vicinity of a boat hull during cleaning, more follow-up sampling is necessary to identify the actual environmental

consequences of such short term releases. Also, development of recreational marinas in areas with lesser tidal circulation or where other pollutant sources might exist, may result in more significant environmental consequences than those recorded in these studies. This might be the case in the southern portions of San Diego Bay, where tidal flushing is reduced.

It should also be noted that these studies only looked at the water quality impacts of existing marinas, and did not address the short or long term impacts that the actual construction of a marina might have on the various beneficial uses of a bay. The mere construction of a marina may seriously restrict or eliminate certain other uses of a bay, most notably - a salt marsh or wildlife habitat. Such physical impacts must also be considered when evaluating the full environmental impact of any new or expanded marina.



## REFERENCES

- Anderson, C.D. and R. Dalley. 1986. Use of organotins in antifouling paints. Oceans '86 (Proceedings). V.4, 1108-1113. New York: IEEE.
- Belli, S.L. and A. Zirino. 1993. Behavior and calibration of the copper(II) ion-selective electrode in high chloride media and marine waters. Analytical Chemistry. 65, 19: 2583-2589.
- Calabrese A., J.R. Macinnes, D.A. Nelson, and J.E. Miller. 1977. Survival and growth of bivalve larvae under heavy-metal stress. Marine Biology. 41: 179-184.
- Litton, G. 1991. California Regional Water Quality Control Board, Santa Ana Region memo regarding preliminary findings of the underwater hull cleaning study.
- California Regional Water Quality Control Board, Santa Diego Region. 1994. Water Quality Control Plan, San Diego Region.
- Claisse, D. and C. Alzieu. 1993. Copper contamination as a result of antifouling paint regulations? Marine Pollution Bulletin. 26, 7: 395-397.
- Conway, J.B. and L.P. Locke. 1994. Marine fouling and underwater hull cleaning in San Diego Bay. A final report prepared for the California Regional Water Quality Control Board, San Diego Region.
- Dodge, E.F., T.L. Theis. 1979. Effect of chemical speciation on the uptake of copper by *Chironomus tentans*. Environmental Science and Technology. 13: 1287-1293.
- Fischer, E.C., V.J. Castelli, S.D. Rodgers, H.R. Bleile. 1984. Technology for control of marine biofouling: A review. In J.E. Costlow, & R.C. Tipper, (Eds.). Marine Biodeterioration: An Interdisciplinary Study. 261-299. Annapolis, MD: Naval Institute Press.
- Flemming, C.A., J.T. Trevors. 1989. Copper toxicity and chemistry in the environment: A review. Water, Air, and Soil Pollution. 44: 143-158.
- Gerchacov, S.M. and L.R. Udey. 1984. Microfouling and Corrosion. In J.E. Costlow, & R.C. Tipper, (Eds.). Marine Biodeterioration: An Interdisciplinary Study. 82-87. Annapolis, MD: Naval Institute Press.
- Grovhoug, J.G., P.F. Seligman, G. Vafa, and R.L. Fransham. 1986. Baseline measurements of butyltin in U.S. harbors and marinas. Oceans '86 (Proceedings) V4: 1283-1288. New York. IEEE.
- Johnston, R.K. 1990. Use of marine fouling communities to evaluate the ecological effects of pollution. Technical Report 1349. Naval Oceans System Center.

Kenis, P., A.R. Zirino, C. Clavell. 1978. Automated Anodic Stripping Voltammetry for the Analysis of Copper, Zinc, Lead, and Cadmium for Environmental Monitoring. Technical Report 243. Naval Oceans System Center.

Krett Lane, S.M. 1990. Productivity and Diversity of Phytoplankton in Relation to Copper Levels in San Diego Bay. Technical Report 533. Naval Oceans System Center.

Loeb, G.I., D. Laster, T. Gracik, D.W. Taylor. 1984. The influence of microbial fouling films on hydrodynamic drag of rotating discs. In J.E. Costlow, & R.C. Tipper, (Eds.). Marine Biodeterioration: An Interdisciplinary Study. 222-228. Annapolis, MD: Naval Institute Press.

Ludgate, J.W. 1987. The economic and technical impact of TBT legislation on the USA marine industry. Oceans '87 (Proceedings) V. 4, 1309-1313. New York: IEEE.

Mellouki, A., A. Bianchi, A. Perichaud, and G. Sauvet. 1989. Evaluation of antifouling properties of non-toxic marine paints. Marine Pollution Bulletin. 20, 12: 612-615.

Nichols, J.A. Antifouling paints: Use on boats in San Diego Bay and a way to minimize adverse impacts. Environmental Management. 12, 2: 243-247.

Preiser, H.S. and D.R. Laster. 1981. On optimization of underwater hull cleaning for greater fuel economy. Naval Engineers Journal. 45-52.

Reimer, C.E. 1992. Geochemical control of toxicant release rates: NOSC program description. San Diego Bay 1992 Annual Report. 2-65. San Diego Interagency Water Quality Panel.

Sunda, W. and R.L. Guillard. 1976. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. Journal of Marine Research. 34, 4: 511-529.

United States Environmental Protection Agency. 1985. Ambient Water Quality Criteria for Copper - 1984. Office of Water Regulations and Standards Division, Washington, DC. EPA 440/5-84-031.

Valkirs A.O., B.M. Davidson, L.L. Kear, R.L. Fransham, A.R. Zirino, and J.G. Grovhoug. 1994. Environmental Effects from In-Water Hull Cleaning of Ablative Copper Antifouling Coatings. Technical Report 2662. Naval Oceans System Center.

VanderWeele, D. and R. Ford. 1994. The effects of copper on the bivalve mollusc *Mytilus edulis* and the amphipod crustacean *Grandidierella japonica* in Shelter Island Yacht Basin, San Diego Bay, California. An Interim Report prepared for California Regional Water Quality Control Board, San Diego Region. 24pp.

Young, D.R., Alexander, G.V., and McDermott-Ehrlich, D. 1979. Vessel-related contamination of southern California harbors by copper and other metals. Marine Pollution Bulletin. 10, 2:50-56.

Zamuda D. and Sunda W.G. 1982. Bioavailability of dissolved copper to the American oyster *Crassostrea virginica*. I. Importance of chemical speciation. Marine Biology. 66: 77-82.

Zirino, A., Lieberman, S.H., and Clavell, C. 1978. Measurement of Cu and Zn in San Diego Bay by automated anodic stripping voltammetry. Environmental and Science and Technology. 12, 1: 73-79.

